SYNTHESIS AND CHARACTERIZATION OF A NOVEL CARBOCYCLIC ALLENE COMPLEX OF IRON

BY

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1982

to my wife and children,

Colleen, Wendy, and Micah,

for their love and understanding

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Chairman: William M. Jones
Major Department: Chemistry

The smallest stable carbocyclic allene is 1,2-cyclononadiene. As one would anticipate as the carbocyclic allene ring is decreased in size, the stability is also decreased. In contrast, transition metal complexes of Pt have been employed to stabilize these strained carbocyclic allenes. Here, it was found that treatment of dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron [(7-methoxy-1-cycloheptenyl)Fp] with trimethylsilyl trifluoromethanesulfonate gave a 71% yield of dicarbonyl-η^5-cyclopentadienyl-η^2-(1,2-cycloheptadienyl)-iron trifluoromethanesulfonate as a crystalline solid.

Examination of the ^{1}H NMR, at low temperatures, revealed the fluxional behavior of the metal, Fp, associated with known Fp allene complexes. Furthermore, the activation energy, $\Delta G^{\ddagger}$, for the interconversion, [1,2]Fp shift, of the isomeric allene complexes was observed at 28°C with a $\Delta G^{\ddagger}$ of 13.9 ± 0.2 kcal/mole. Further proof of the

structure of the carbocyclic allene Fp complex was obtained by the use of spin saturation transfer which allowed additional examination of the [1,2]Fp shift at low temperatures.

The ^{13}C NMR, at low temperatures, revealed that the carbocyclic allene Fp complex shows some metallocyclopropyl character, as seen in the Pt carbocyclic allene complexes, as characterized by the extreme upfield shifts of the C_1 + C_2 carbons of the carbocyclic allene.

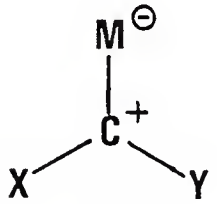
Contrary to earlier reports on the addition of MeO^- to acyclic allene Fp complexes, it was found that addition of EtOH occurred on the C_1 carbon of the η^2-allene fragment. This generated the sigma complex, dicarbonyl-η^5-cyclopentadienyl-η^1-(7-ethoxy-1-cycloheptenyl)iron, in a 54% yield.

A second attempted approach to the carbocyclic allene complex was through the generation of the cyclopropanonyl-iron sigma complex. Previously, it was reported that the parent cyclopropanol complex of Fp would not decarbonylate to the corresponding sigma complex. Contrary to these earlier reports, photodecarbonylation of the corresponding acyl complexes gave excellent yields of the desired sigma complexes. However, attempts to generate the desired alpha-halo sigma complexes were unsuccessful, thus not allowing entrance into the allene manifold.

Unfortunately, methoxy abstraction from dicarbonyl-η^5-cyclopentadienyl-η^1-(6-methoxy-1-cyclohexenyl)iron with $Me_3SiOSO_2CF_3$ did not afford the carbocyclic allene complex but rearranged products derived from carbocation intermediates.

CHAPTER I
INTRODUCTION

The synthesis, bonding, and structure of transition metal complexes of carbenes have been investigated and reviewed many times over the last few years.[1-4] The bonding within complexes containing hetero atoms or π-systems which are alpha to the carbene carbon can be considered in terms of three principal canonical forms (1, 2, 3).[1-3] Resonance form 1



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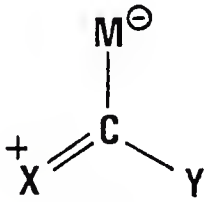

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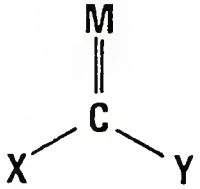

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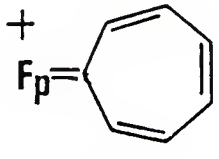
shows no interaction of the vacant p_z orbital of the methylene carbon while resonance form 2 represents the vacant p_z carbene orbital interacting with the π-system (4, 5)[5,6] or the lone pair on the hetero atom



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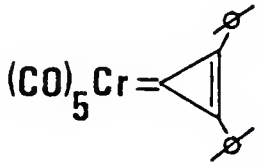

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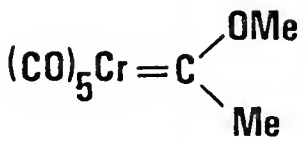
Fp = $C_5H_5Fe(CO)_2$

(X or Y) of the ligand (6, 7, 8).[7-9] Resonance form 3 represents



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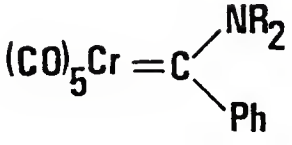

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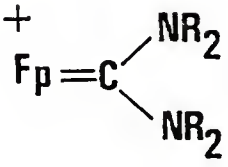

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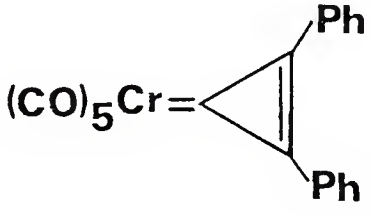
interaction of the vacant p_z orbital with the d orbitals of the metal. The energy difference between the metal d orbital and that of the p_z orbital influences the contribution of resonance form 3. This so called "back bonding" can be assessed with the use of x-ray crystallographic and spectroscopic data.

The first transition metal complex of a carbene (5) with a (4n+2)-π-system (n=0) was reported by Öfele[6] in 1969. More recently the



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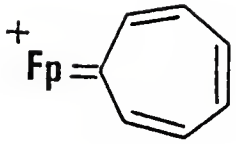
synthesis of a series of aromatic transition metal complexes (4 and 9) with (4n+2)π-electrons (n=1) was achieved by Allison and co-workers.[5]



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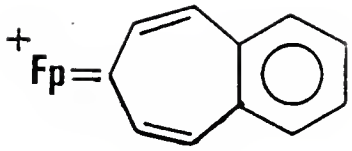

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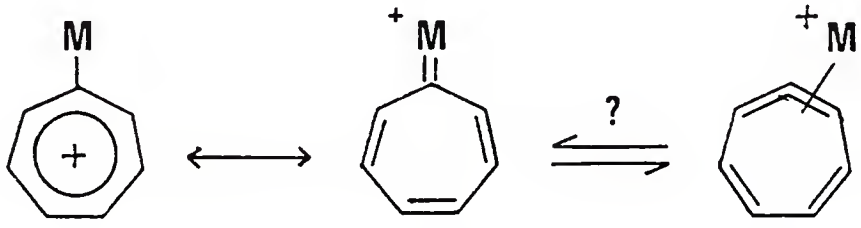
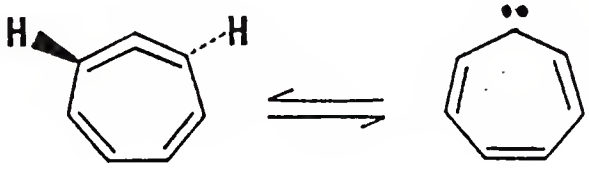
In principle cyclic conjugated ligands such as C_7H_6 could exist in either a carbene (10) or allene form (11). In the case of such complexes



10 11

as (4) and (9) it is clear from the NMR spectra that the ligand is complexed in the form of the carbene rather than an allene;[5] even in the case where a $P(C_4H_9)_3$ derivative was prepared the carbene form was favored.[11] This is notable because recent evidence (theoretical and experimental) has pointed to the probability that in nonmetallic compounds the twisted allene structure (12) is lower energy than the carbene structure (13).[10]

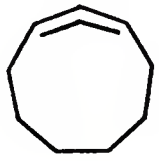


12 13

To date, evidence for an example of a metal-cycloheptatetraene (11) has not been found. This indicates that in the cases reported to date,

either the carbene complex (10) is of lower energy than the allene (11) or the method of synthesis leads to a higher energy but kinetically stable form.

The question arises, then, can transition metal complexes of carbocyclic allenes (either conjugated or nonconjugated) be prepared? A review of the literature reveals that carbocyclic allenes are generally very reactive and rather unstable molecules.[12-17] The smallest stable carbocyclic allene is 1,2-cyclononadiene (14).* If the carbocyclic ring



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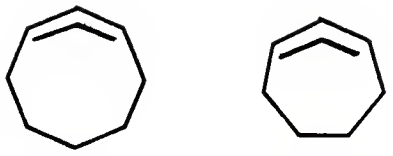
is decreased in size, the strain within the ring is increased; thus 1,2-cyclooctadiene (15) can only be observed spectroscopically (at low temperature) and trapped, whereas 1,2-cycloheptadiene (16)[18,19] can be generated and trapped but has never been observed (spectroscopically).

* An idealized (C=C=C) angle of 180° and torsional angle of 90° dictates the requirement for relatively large rings.



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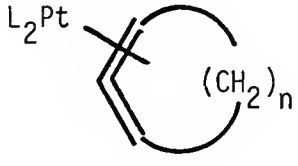
On the other hand, in 1972, Visser and Ramakers[20] synthesized platinum complexes (17, 18, 19) of a number of carbocyclic allenes and succeeded in isolated stable crystalline products for cyclic allenes as



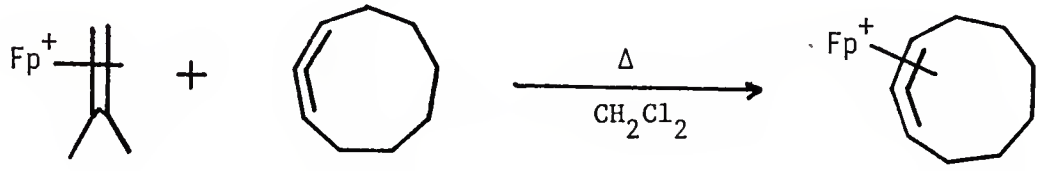
17 n=6
18 n=5
19 n=4

few as seven carbons. Preparation of these carbocyclic allene complexes (20) was achieved by the generation of the carbocyclic allene (21)

21 22 20

(dehydrohalogenation of the bromocycloalkenes at low temperatures)[20] in

the presence of (22). These complexes were presumably formed by addition to the vacant coordination site of the metal followed by the loss of ethylene.[21] One iron complex of a carbocyclic allene has also been reported. In this case, Foxman and co-workers[22] were able to prepare a stable carbocyclic allene complex (23) (93%) by the exchange reaction of (24) with the stable carbocyclic allene (14); the smaller carbocyclic

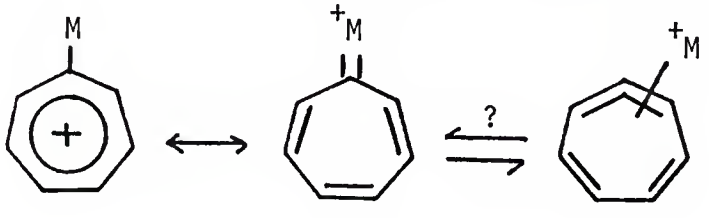


24 14 23

allenes would not work here due to the high temperature needed to generate the metal allene complexes.

Other carbocyclic allenes (i.e., cyclonona-1,2,6-triene and cyclodeca-1,2,6,7-tetraene)[23,24] are known to form 1:1 complexes with silver nitrate or with cuprous chloride; however these are not applicable here.

Reflecting back on the interconversion of (10) and (11) one sees that this is a specific example of a much broader question of the



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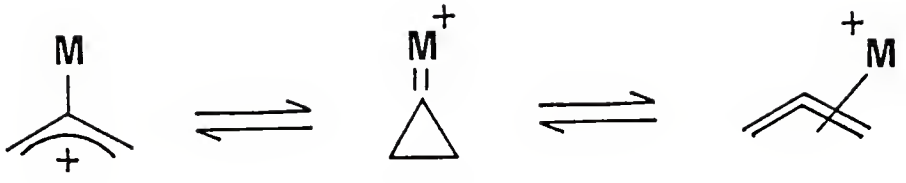
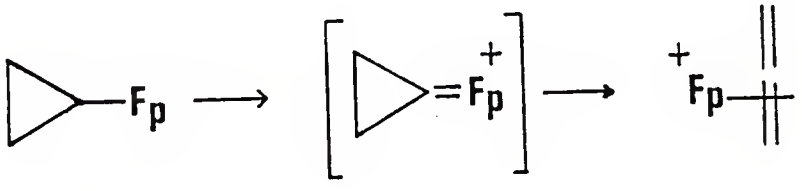
energetics and valence isomerization of the types of metal complexes (25), (26), and (27). Here the isomeric form (25) shows a sigma bond



25 26 27

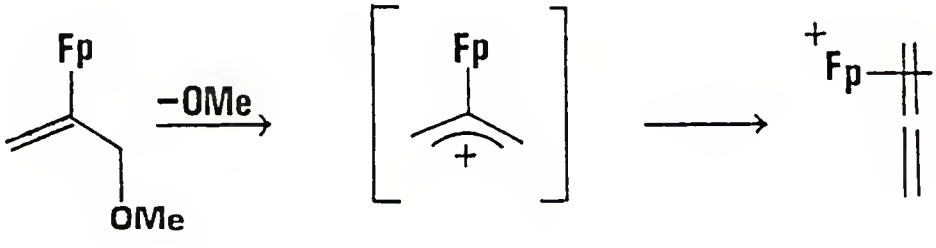
with virtually no back bonding possible, a sigma bond in (26) with extensive back bonding and a π-bond in (27).

A review of the literature reveals only a few examples of these kinds of interconversions. Recently Cohen and co-workers[25] found that hydride abstraction from (28) gave the allene complex (29), presumably



28 30 29

via (30). Lennon and co-workers[26] found that methoxy abstraction from (31) also gave the allene (29). However, here the iron may assist in

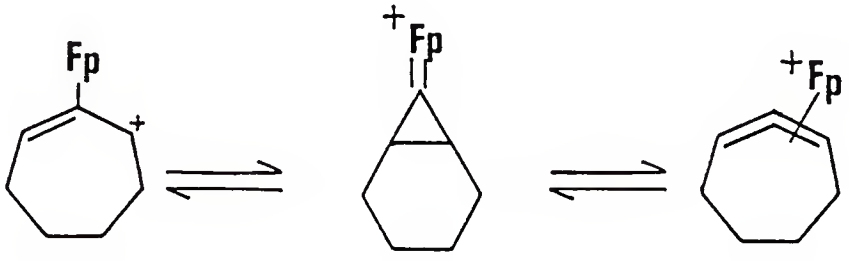


31 32 29

the direct loss of the methoxy so that the sigma complex (31) may go directly to the allene complex (29), bypassing the cation (32), via an anti Fp assistance.

To study the interconversion of (25), (26), and (27) ideally one would like to enter a given manifold at one of the higher energy forms and then observe its collapse to one of the more stable complexes (i.e., (30) to (29), the more stable product).

It was the aim of this research to study the interconversion of Fp complexes of small carbocyclic valence isomers (33, 34, 35) entering a given manifold at one of the higher forms and observing its collapse to

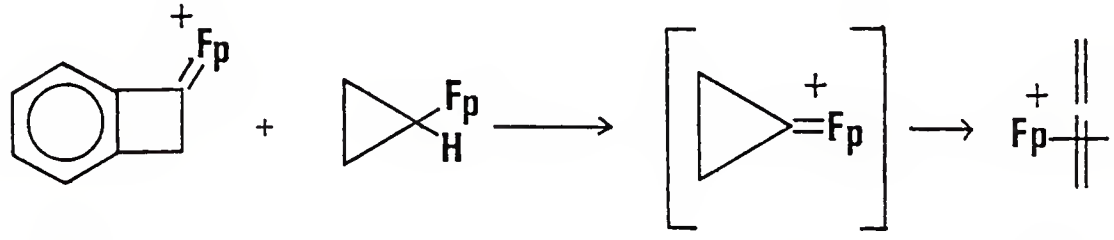


33 34 35

a more stable complex. Since the platinum complex of 1,2-cycloheptadiene (19) has been trapped, we elected to begin with attempts to generate the cyclopropylidene and the cycloheptenyl Fp complexes (34) and (35), respectively, to see if they would collapse to the allene form (35).

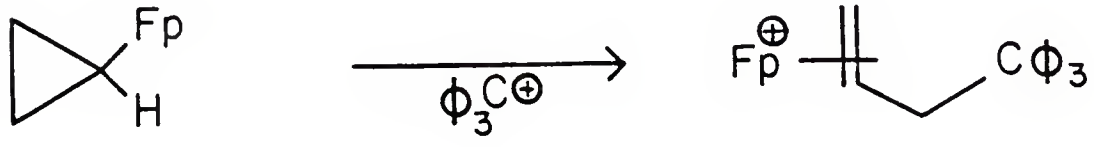
CHAPTER II
ATTEMPTS TO GENERATE CYCLOPROPYLIDENE COMPLEXES OF IRON

In principle, the simplest method to generate cyclopropylidene complexes of Fp, (30), would be simple hydride abstraction from appropriately substituted sigma Fp complexes. And, indeed, one example of such a reaction has been reported using an exotic reagent (36) with the sigma complex (28).[25] However, hydride abstraction does not



36 28 30 29

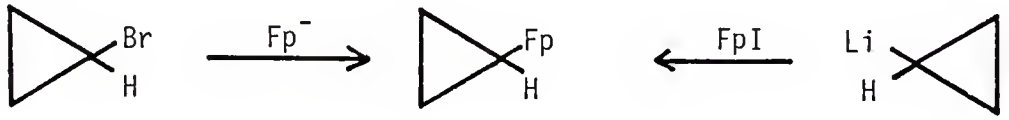
appear to be a generally useful method for preparing this kind of complex. For instance, Cutler and co-workers[27] have found that attempts to abstract hydride from (28) with trityl did not give the desired complex (30), but rather the addition product (37).



28 37

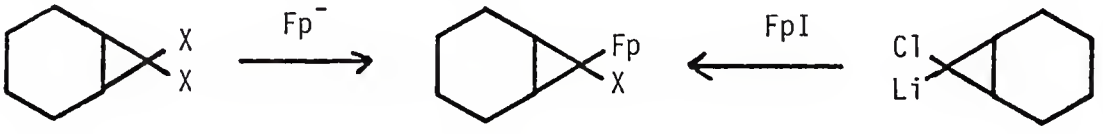
We therefore turned our attention to the synthesis of sigma cyclopropyl Fp complexes in which the alpha-hydrogen has been replaced by a better leaving group such as a halogen or a methoxy group.

The first synthetic approach chosen for the synthesis of sigma bonded alpha-halocyclopropyl Fp complexes was patterned after that of Culter and co-workers,[27] who found that the parent complex could be prepared by either treatment of cyclopropyl bromide (38) with Fp anion or by the alkylation of FpBr with cyclopropyllithium (39). By analogy,



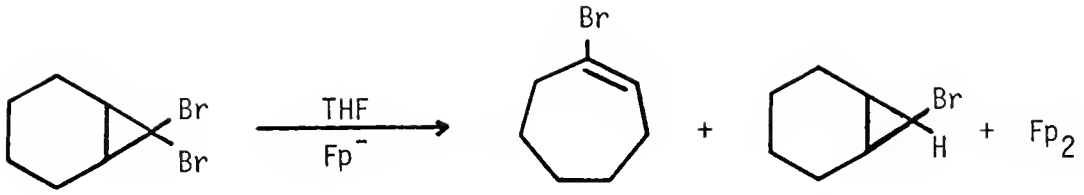
38 28 39

either the reaction of (40a) or (40b) with Fp anion or the reaction



	X		X	
40a	Br	42a	Br	41
40b	Cl	42b	CL	

(41) with FpI, could result in the formation of (42a) or (42b). Unfortunately, when (40a) was added to a suspension of Fp anion (at 0°C) (42a) was not observed; only (43), (44), (45) and unreacted



40a 43 44 45

starting material were recovered. Likewise, when (40b) was treated with Fp anion, under the conditions as above, only (45), (46)

40b 46 45

and unreacted starting material were found. Formation of (44) and (46) finds analogy in the report of Marten and co-workers,[28] who found that the reaction of (47) with Fp anion gave the reduced

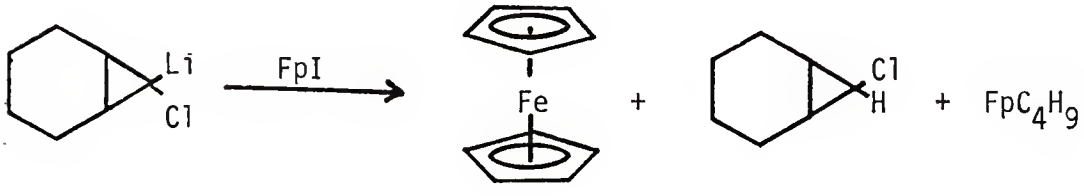
47 48 45

product (48). Since the addition of the Fp anion to the dihalo compound gave only the reduction products, an attempt was made to

generate (42b) by the reaction of the anion (41) with FpI. Unfortunately, again all attempts failed. Isolation of the products gave only (46),

41 42b

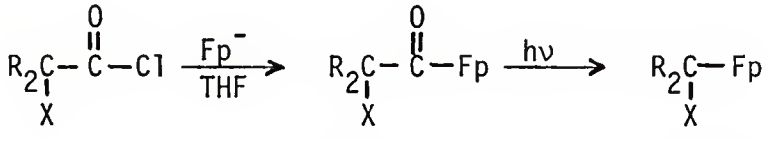
(49), and (50), the latter presumably arising from the reaction of



41 49 46 50

unreacted BuLi with FpI.

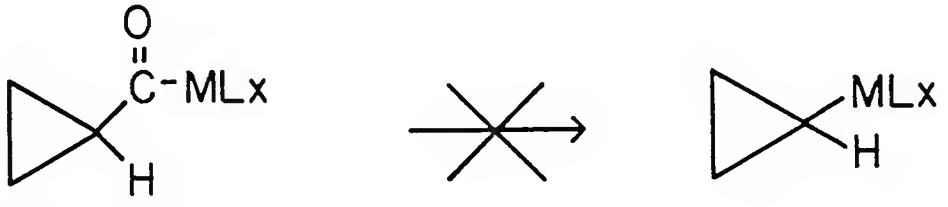
Since alpha-substituted Fp complexes could not be prepared by either of the above methods, a third approach was attempted as illustrated below:



Acyl Complex Sigma Complex

It is well known that metal anions readily react with acid chlorides to generate the corresponding acyl metal complexes which,

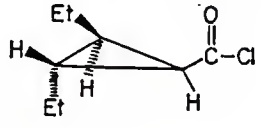
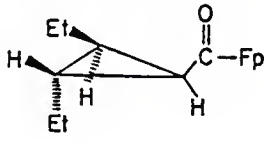
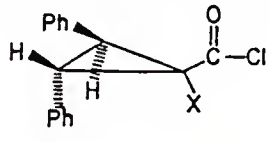
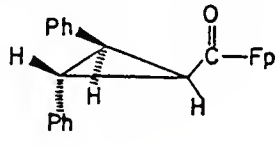
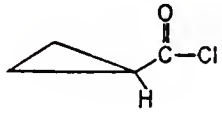
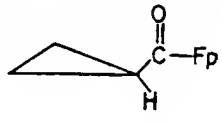
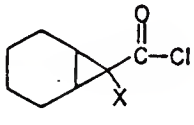
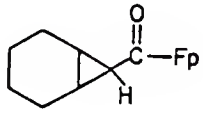
in turn, can normally be decarbonylated (either thermally or photochemically) to the corresponding sigma metal complex.[29] Unfortunately, Bruce and co-workers[30] had reported that attempts to decarbonylate the acyl cyclopropyl metal complexes (51a-d) were unsuccessful. These

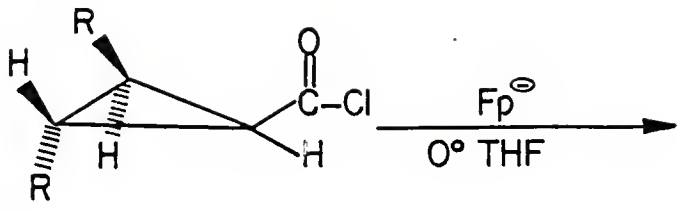


51 (a-d)
a) MLx = $Mn(CO)_5$ b) MLx = $Re(CO)_5$
c) MLx = $Fe(CO)_2Cp$ d) MLx = $Ir(CO)Cl_2(PPh_3)_2$

attempts included thermolysis, photolysis and reaction with $(Ph_3P)_3RhCl$[31-33] (known to be an efficient abstractor of carbon monoxide). Despite their failure, we noted that their attempts were limited to the parent complexes and suspected that the substituents on the cyclopropyl rings of the Fp complexes might cause these complexes to behave differently. We therefore undertook the synthesis of a series of model alpha-hydrogen substituted cyclopropyl Fp complexes to see if effective decarbonylation conditions could be found.[34] The synthesis of the desired substituted acyl complexes (52), (53)[35] and (54) was found to be straightforward. Treatment of the substituted cyclopropyl acid chlorides (55), (56) and (57) with Fp anion (at 0°C) gave poor to excellent yields (Table 1) of the desired metal complexes (52), (53) and (54).

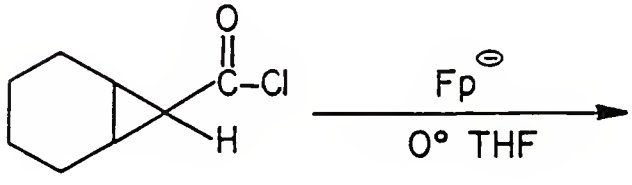
Table 1. Yields from the reactions of Fp^- with the corresponding acid chlorides.

Reaction of $Fp^{\ominus}$ and Acyl Halide	yield %	Acyl Complex
	63 %	
	X H 77 % Br 15 %	
	20 %	
	X H 18 % Cl 17 % Br 3 %	



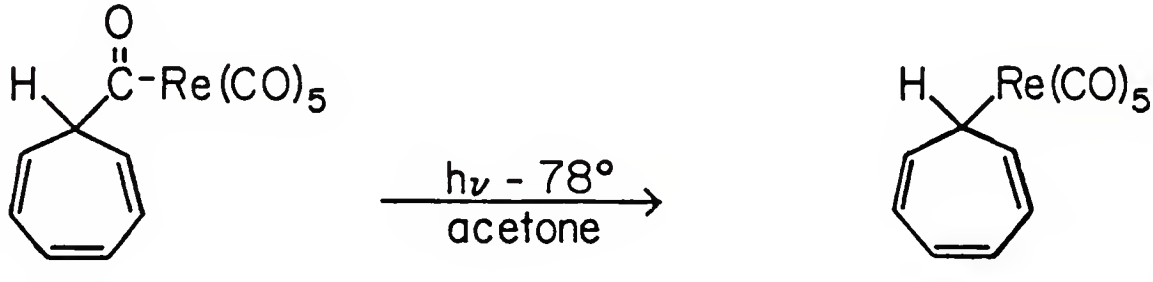
	R
55	ϕ
56	E+

	R
52	ϕ
53	E+



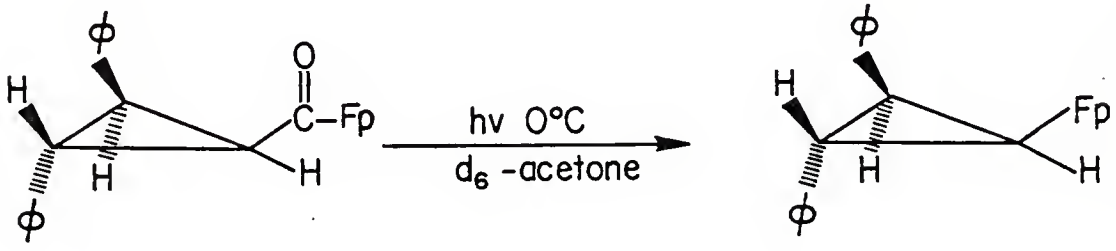
57 54

Since the unsuccessful attempts to photodecarbonylate the parent acyl Fp complex (51c) had been carried out in petroleum ether (or neat) an alternate solvent was sought. Recently, Graham and Heinekey[36] reported that the photolysis of (58) in acetone (at -78°C) gave the corresponding sigma complex (59) in a good yield (60%). We therefore carried out our photodecarbonylation in acetone and were gratified to



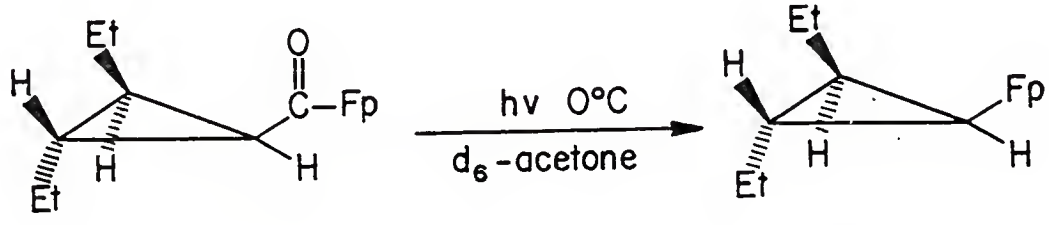
58 59

find that (52) underwent smooth decarbonylation (at 0°C; in 2 hours) to give an excellent yield (97%) of the desired sigma complex (60).[35]

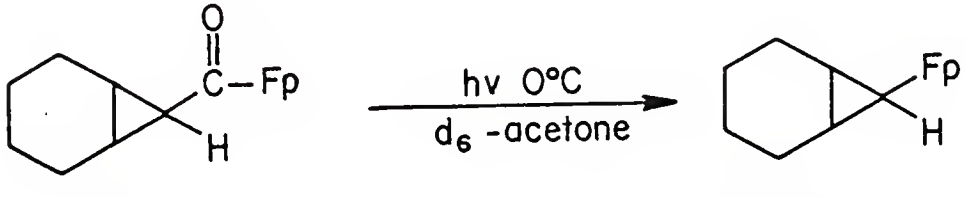


52 60

Likewise photolysis of (53)[35] and (54), under the same conditions, also gave the alkyl complexes (61) and (62), albeit the latter in only 15% yield.



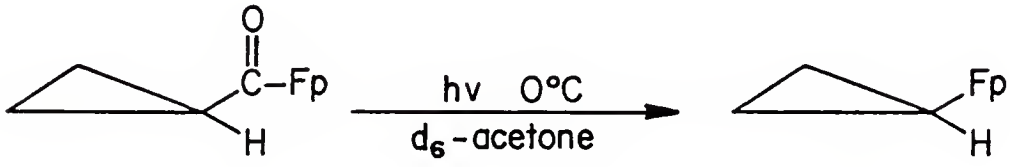
53 61



54 62

As a result of these encouraging results, photodecarbonylation of the parent acyl Fp complex (51c) was also attempted in d_6-acetone.

Indeed, photolysis of (51c), at 0°C for 10 minutes, led to the formation of a new metal complex (a new Cp resonance appeared at δ 4.90).



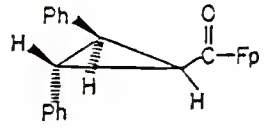
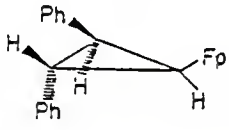
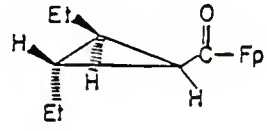
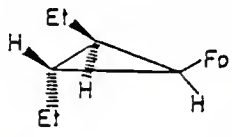
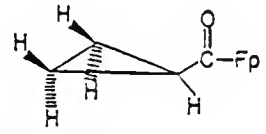
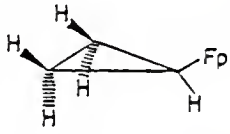
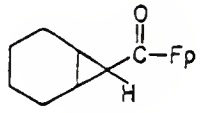
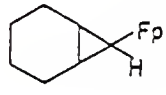
51c 28

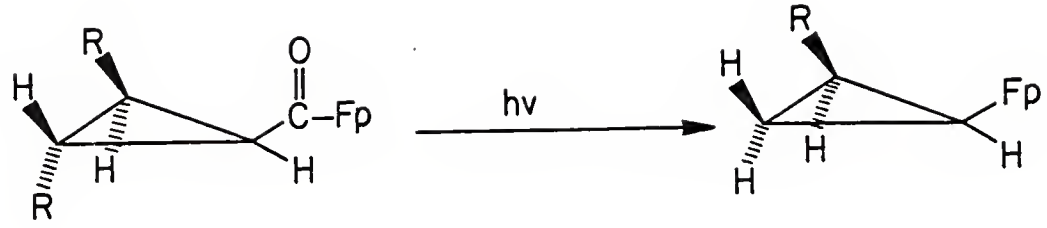
After photolysis for one hour and 10 minutes the ^1H NMR showed nearly complete loss of starting material. The solution was worked up at this time to give the desired Fp complex (28) in a 75% yield.

Since our photolyses were conducted in d_6-acetone, while those of Bruce and co-workers[30] had been carried out in petroleum ether (or neat), we desired to photolyze (51c) and (52) in petroleum ether to see if this led to reduced yields. Indeed, in both cases even though the photolysis gave the desired sigma complexes (28) and (60) the yields* in each case were significantly lower than in d_6-acetone. The photolyses were also carried out in d_6-benzene. Again each acyl complex gave the desired sigma complex but in this case yields were between those observed in d_6-acetone and petroleum ether (Table 2).

* The product (28) may have not been detected by Bruce and co-workers[30] due to low yield (16%).

Table 2. Yields from photolysis of the corresponding acyl complexes.

Acyl Complex	Photolysis Solvent	Sigma Complex	yield %
	d_6 - acetone d_6 - benzene Petroleum ether		97 % 64 % 51 %
	d_6 - acetone		75 %
	d_8 - acetone d_6 - benzene Petroleum ether		75 % 52 % 16 %
	d_8 - acetone		52 %

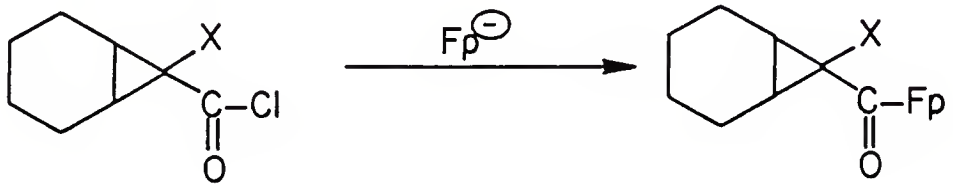


	R
52	ϕ
51c	H

	R
60	ϕ
28	H

Having demonstrated the viability of the decarbonylation step for the model system we then turned our attention to the preparation of alpha-halo acyl Fp complexes.

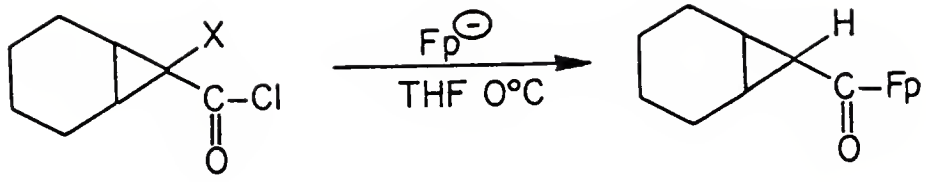
We first attempted to prepare (63) and (64). Unfortunately, in each case reaction of the alpha-halo acyl halide (65 and 66) with Fp



	X
65	Br
66	Cl

	X
63	Br
64	Cl

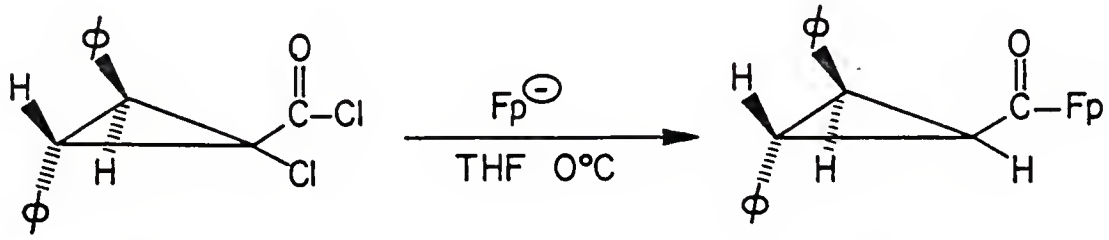
anion resulted not in the formation of the desired metal complexes (63) and (64), but rather the reduced complex, (54).



	X
65	Br
66	Cl

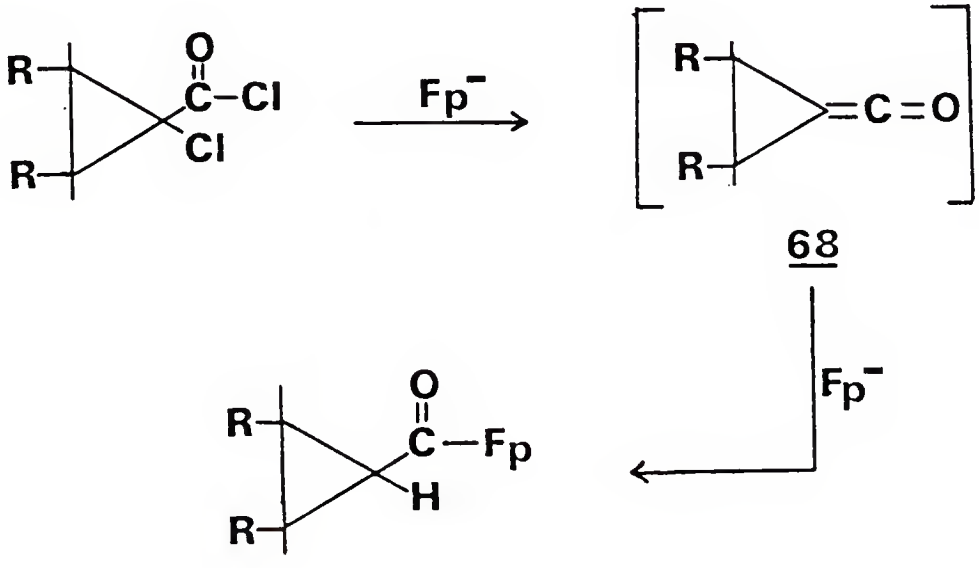
54

This was also found to be the case for the reaction of (67) with Fp anion; again only the reduced product (52) could be isolated.



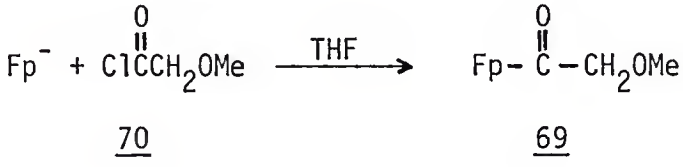
67 52

The mechanism of the reduction is not known. However, one reasonable possibility is shown below.

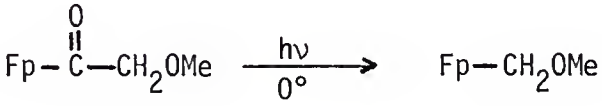


In this mechanism the Fp anion induces elimination to give the ketene (68) which further reacts to give the reduced products.

Since it appeared that alpha-halo acyl chlorides could not be used to prepare the desired carbene precursors, we turned our attention to complexes with a methoxy group in the alpha position. We were optimistic about this as a viable approach because Cutler and co-workers[37] were able to generate the acyl Fp complex (69) by reacting (70) with Fp anion; no reduction occurred. In turn, we were able to photodecarbonylate (69) in d_6-acetone (at 0°C) to give the known sigma complex (71).

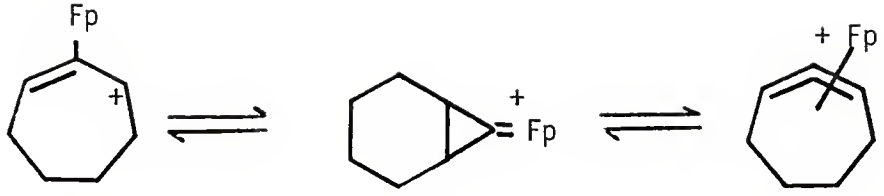


70 69



69 71

We expect that methoxy abstraction may have real potential for the preparation of cyclopropylidene Fp complexes. However, a search of the literature revealed very few alpha-methoxycyclopropyl carboxylic acids and we expect their synthesis to be quite a challenge. Furthermore, concurrent with this work, we were also exploring ways to enter the seven membered ring manifold at the allyl cation (33). Since this

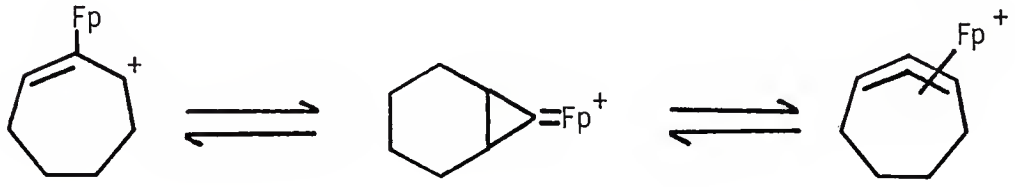


33 34 35

was progressing better than the cyclopropylidene investigation, we turned our attention to this new area.

CHAPTER III
GENERATION OF THE CARBOCYCLIC ALLENE Fp COMPLEX

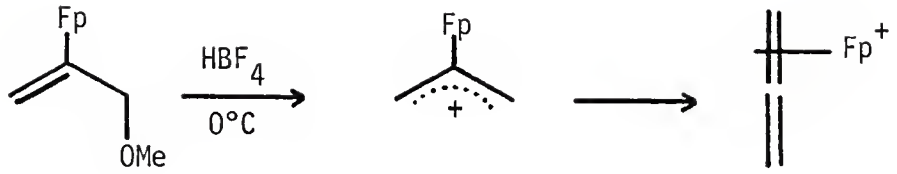
In view of our unsuccessful attempts to generate the cyclopropylidene complex (34) alternate approaches into the valence isomer manifold



33 34 35

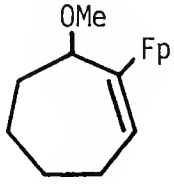
(33, 34, 35) were explored. Ideally one would like to enter this manifold at a higher energy form and observe its collapse to a more stable complex. We therefore undertook an approach aimed at the preparation of the allyl cation complex (33) to see if it would rearrange to the carbocyclic allene (35) or even cyclize to the cyclopropylidene complex (34).

As mentioned before, it was reported some years ago that treatment of the ether complex (31) with $HBF_4 \cdot Et_2O$ gave the stable acyclic allene complex (29),[26] possibly via the allyl cation (32). Applying the same



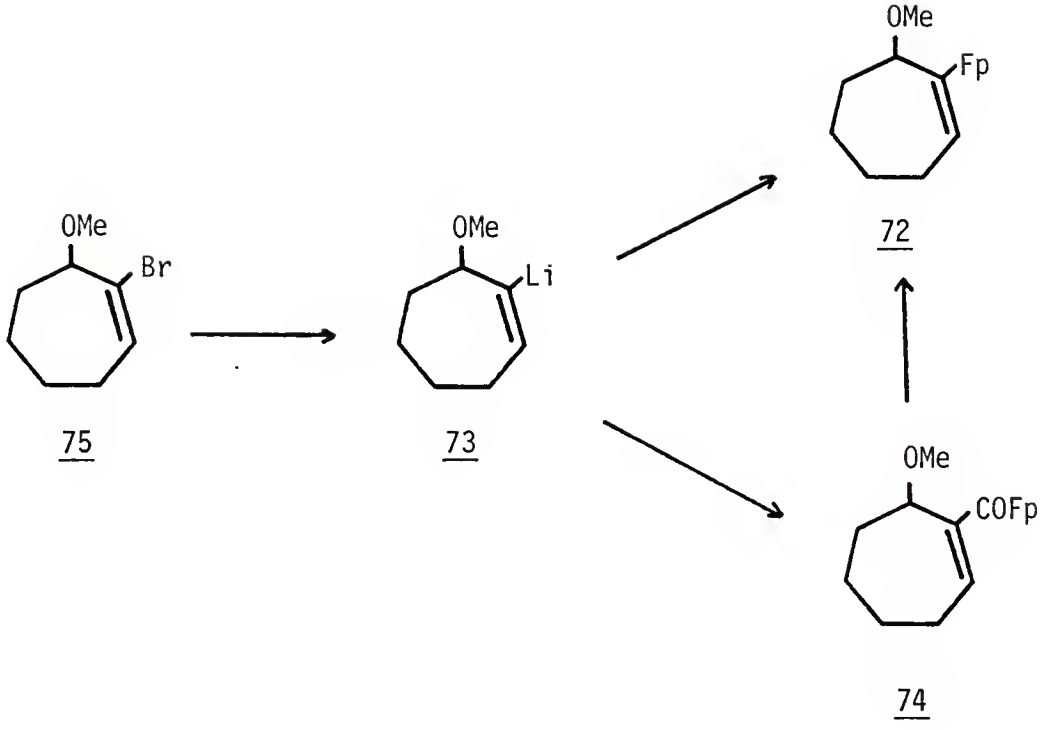
31 32 29

methodology to the carbocyclic system, prepration of (72) was undertaken.



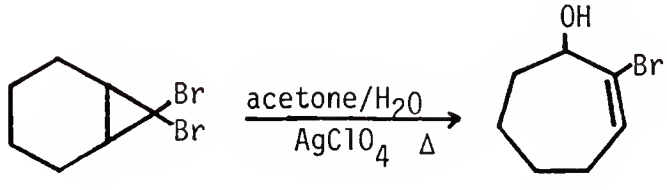
72

In principle (72) could be prepared from (73) by employing the two approaches discussed in Chapter 2 [i.e., either by the alkylation of FpI or chlorocarbonylation of (73) followed by conversion to the sigma complex (72)]. Thus, the synthesis rested on the preparation of (75) (using the logic shown in the following scheme).



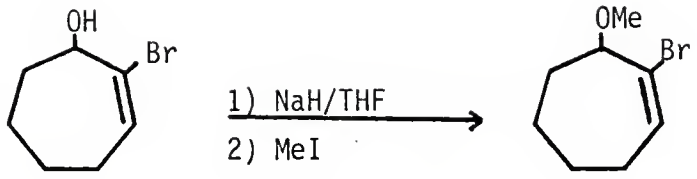
75 73 72 74

Recently, Balci and Jones[38] prepared the alcohol (76) by treatment



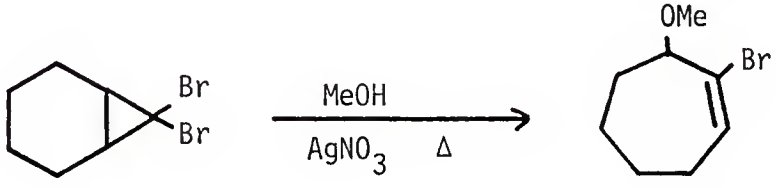
40a 76

of (40a) with $AgClO_4$ in the presence of H_2O/acetone in an 80% yield. With (76) in hand we found that treatment with NaH followed by MeI gave



76 75

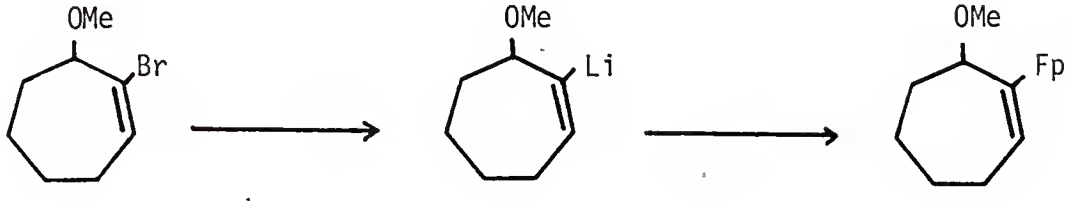
the desired ether (75) in a 41% yield. Later a more direct and higher yield preparation of (75) was achieved by treatment of (40a) with $AgNO_3$*, in MeOH.



40a 75

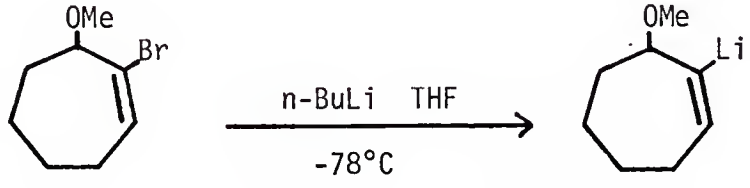
* $AgClO_4$ in MeOH gives a higher yield (97%) but the reaction mixture proved explosive.

The first approach to the synthesis of the carbocyclic sigma complex (72) is shown below:



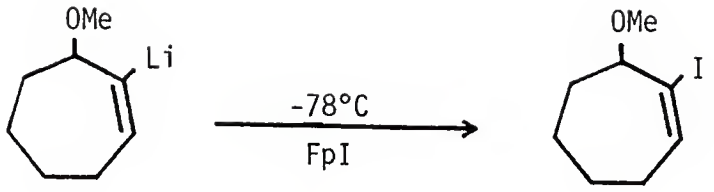
75 73 72

Unfortunately, although treatment of (75) with n-Buli, at -78°C, gave



75 73

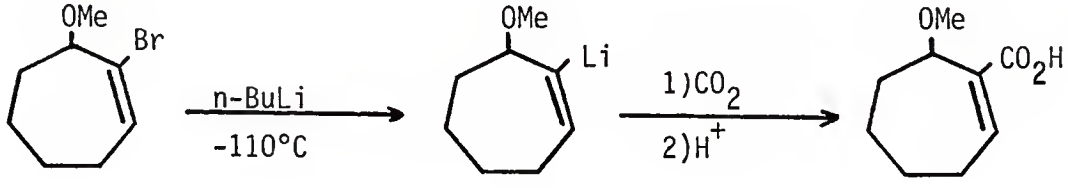
a yellowish solution that was apparently (73), treatment of this solution with FpI at -78°C did not give the desired sigma complex (72), but rather (77) in a 55% yield.



73 77

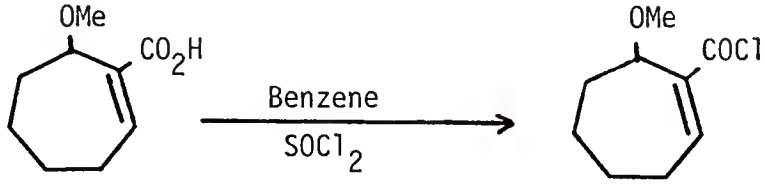
Since the above approach to the desired sigma complex (72) failed, a second approach was attempted as seen in Scheme 1.

Treatment of (75) with n-BuLi at -110°C followed by addition of

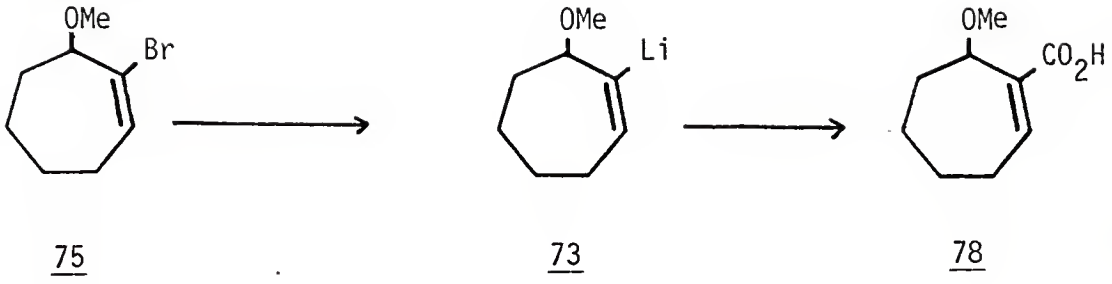


75 73 78

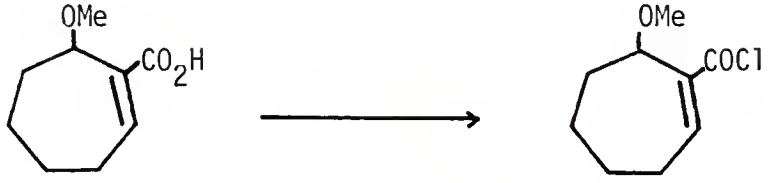
CO_2 and acid work-up gave the acid (78) in a 66% yield. The acid (78)



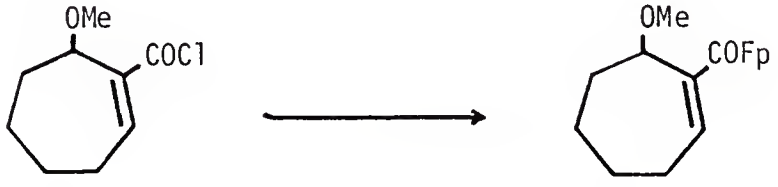
78 79



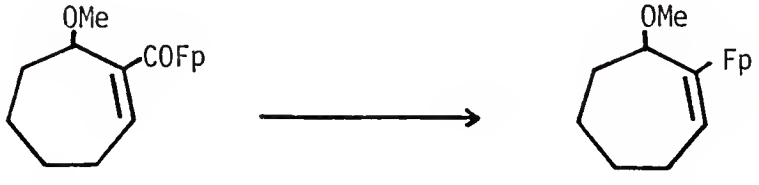
75 73 78



78 79



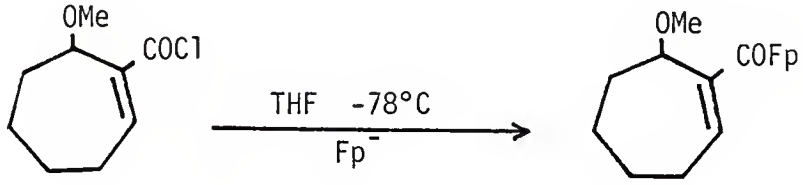
79 74



74 72

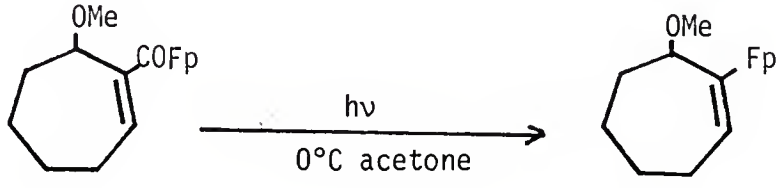
Scheme 1

was then treated with $SOCl_2$ (in benzene) to give the acid chloride (79) in a 70% yield. Addition of the acid chloride (79) to a suspension of



79 74

Fp anion in THF at -78°C gave a 27% yield of the desired acyl complex (74) as an air-sensitive, brownish oil. The ^1H NMR spectrum of (74) is given in Figure 1. Photodecarbonylation of (74) in d_6-acetone at 0°C gave an air-sensitive, brownish oil (72) in a 53% yield. The ^1H NMR spectrum of (72) is given in Figure 2.



74 72

At this point the question arises, will (72), when treated with $HBF_4 \cdot Et_2O$, behave similarly to the model system (31) as reported by Lennon and co-workers?[26] It was found that treatment of (72) with

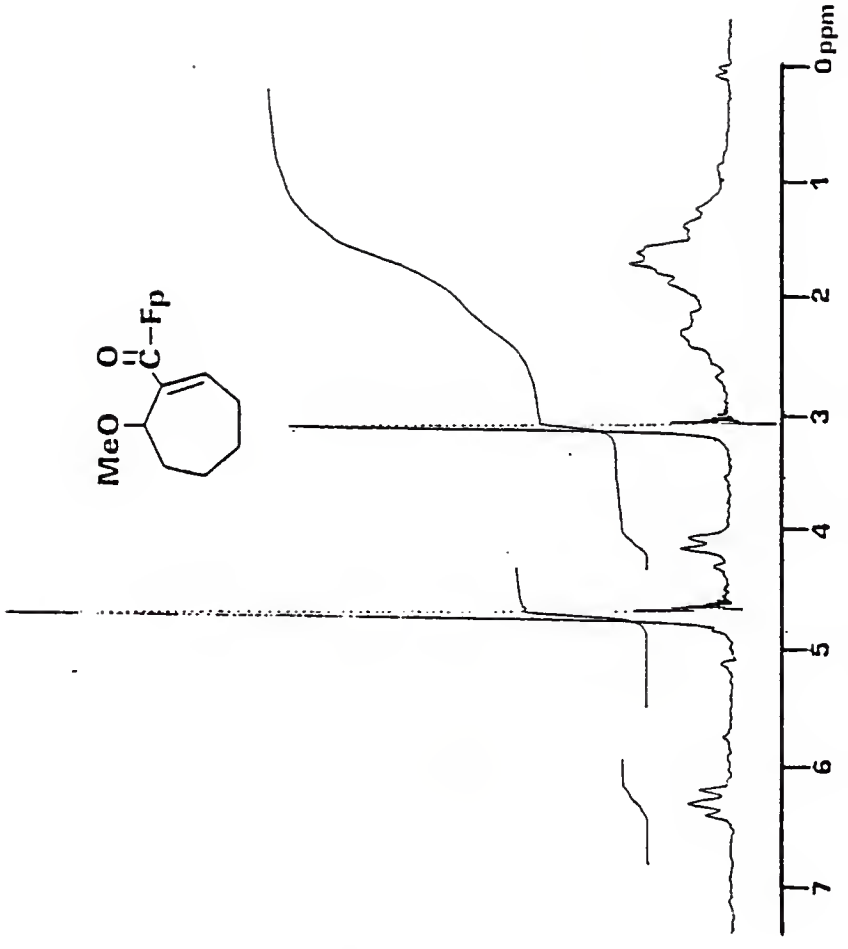


Figure 1. ^{1}H NMR spectrum of (74) in $CDCl_3$.

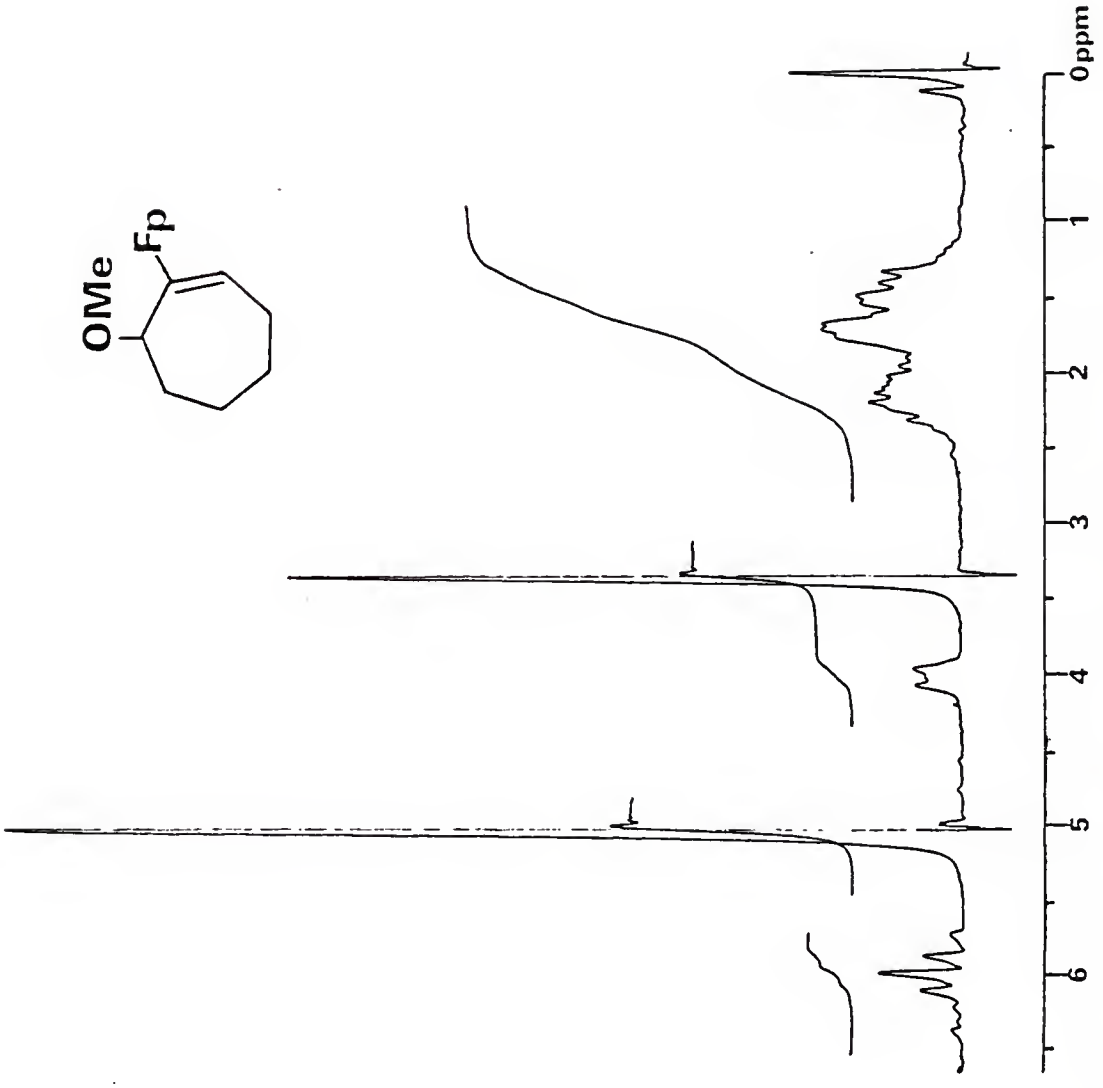
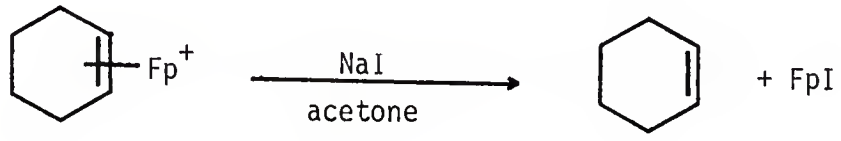
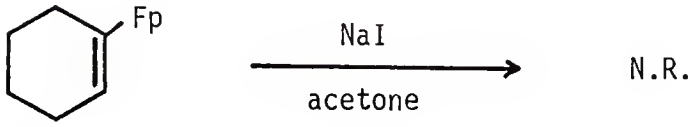


Figure 2. ^{1}H NMR spectrum of (7Z) in $CDCl_3$.

$HBF_4 \cdot Et_2O$ at -78°C gave an immediate precipitate which, from the low field Cp resonances (δ ~5.65) in the ^1H NMR spectrum (Figure 3) suggested the formation of π-complexes of Fp. This downfield shift is consistent with known π-complexes of Fp as indicated in Table 3. It is well known that π-complexes of Fp undergo facile displacement of olefinic ligand by halide ions, usually I^-, whereas sigma complexes of Fp are unreactive.[39-41] The precipitate from above was therefore





treated with NaI in d_6-acetone to immediately give a color change which upon work-up revealed that FpI had been produced. Further examination, glpc, revealed that the ligands that had been displaced were cycloheptanone (80) or its precursor, cycloheptene (81), and trace amounts of 1,3-cycloheptadiene (82) by GC/MS.

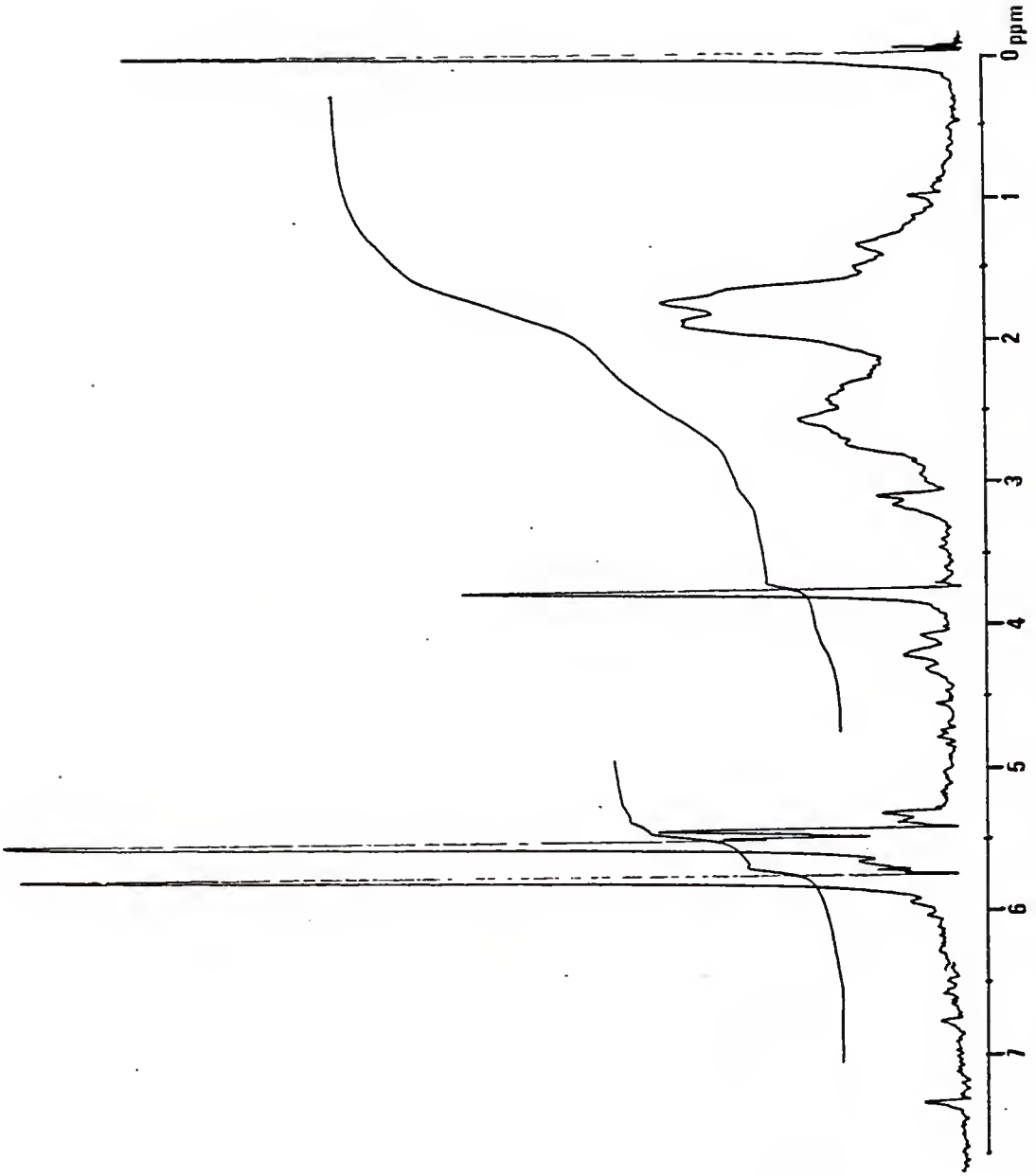
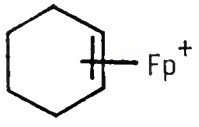
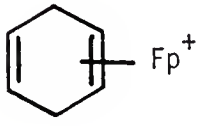
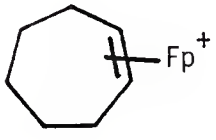
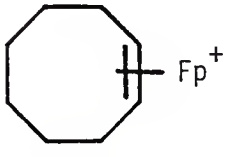
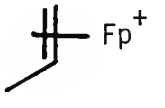
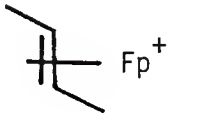


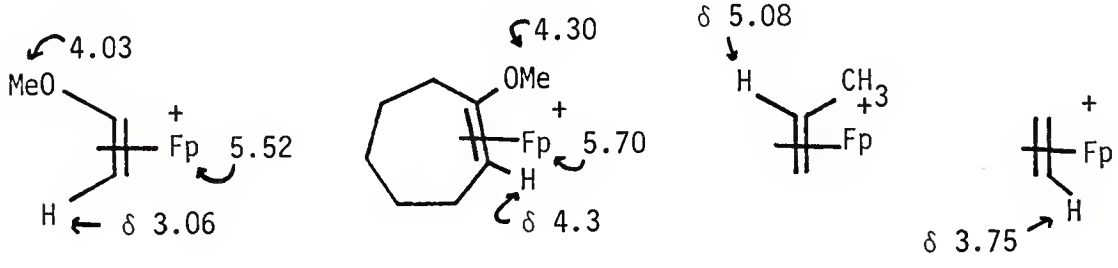
Figure 3. ^{1}H NMR spectrum of the crude products from the addition of HBF_4 to (72).

Table 3. ^{1}H NMR resonances of the Cp of π-complexes.

	Cp (in ppm's)
	5.78
	5.62
	5.60
	5.61
	5.65
	5.62
	5.67

One possible mechanism to rationalize these products is seen in Scheme 2.

Addition of $HBF_4 \cdot Et_2O$ to (72) could initially generate two different intermediates (33) and (83). Simple protonation of the double bond of (72) would generate the carbocyclic carbene (83) which could rearrange to give the π-complex (84). A closer examination of the ^1H NMR spectrum of the crude protonation product (Figure 3) reveals a singlet at 3.80 ppm, a triplet at 4.30 and a singlet at 5.70 which is a good indication of structure (84) since (85) shows similar resonances at 4.03 ppm, 3.06 and 5.52. It should be noted that the resonances at



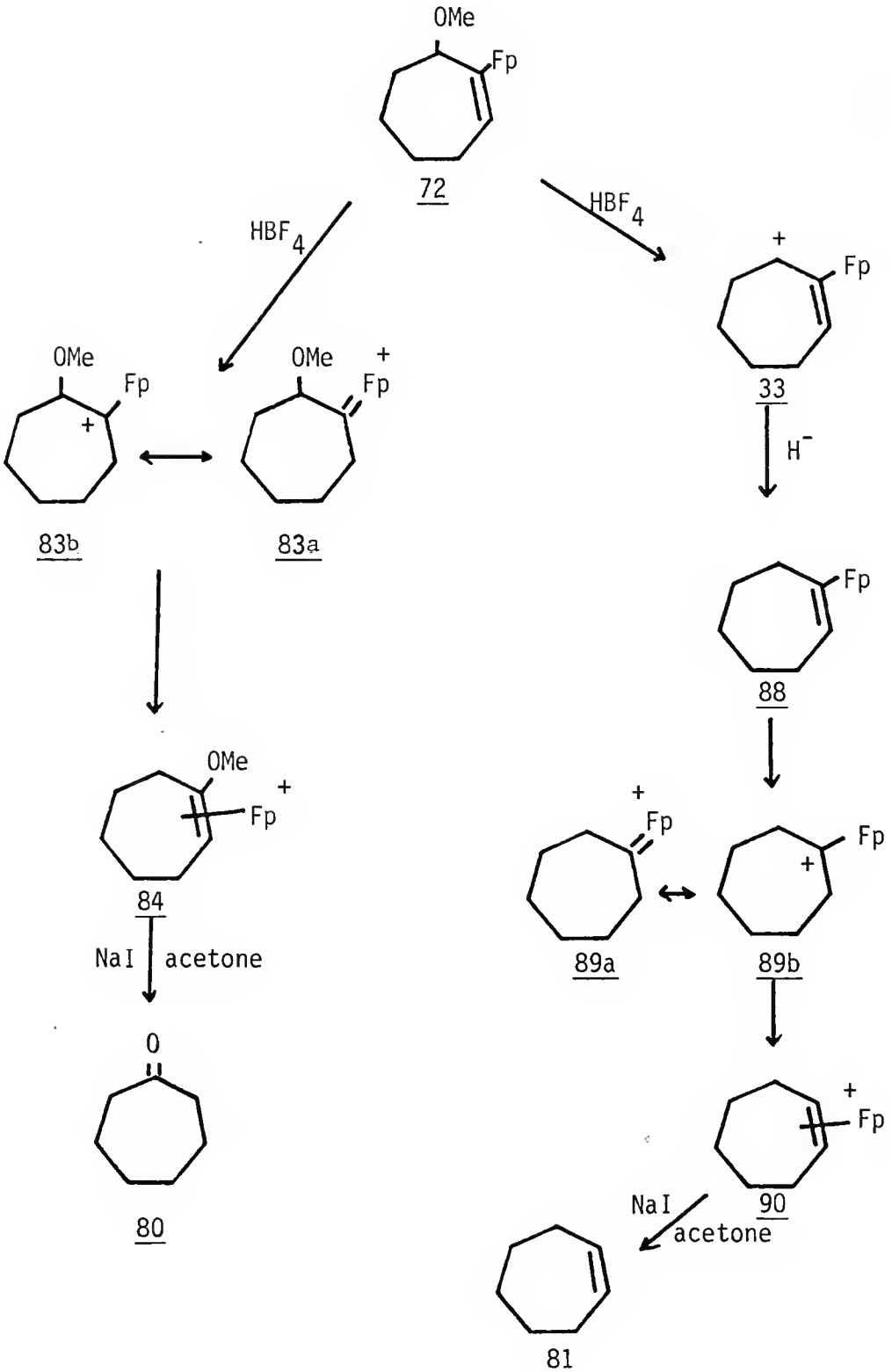
85 84 86 87

3.06 ppm in (85) and 4.30 ppm in (84) are somewhat different, but this difference is not unexpected since alkyl substitution in (86) vs. the parent complex (87)[42] causes a comparable difference in the chemical shifts of the protons.

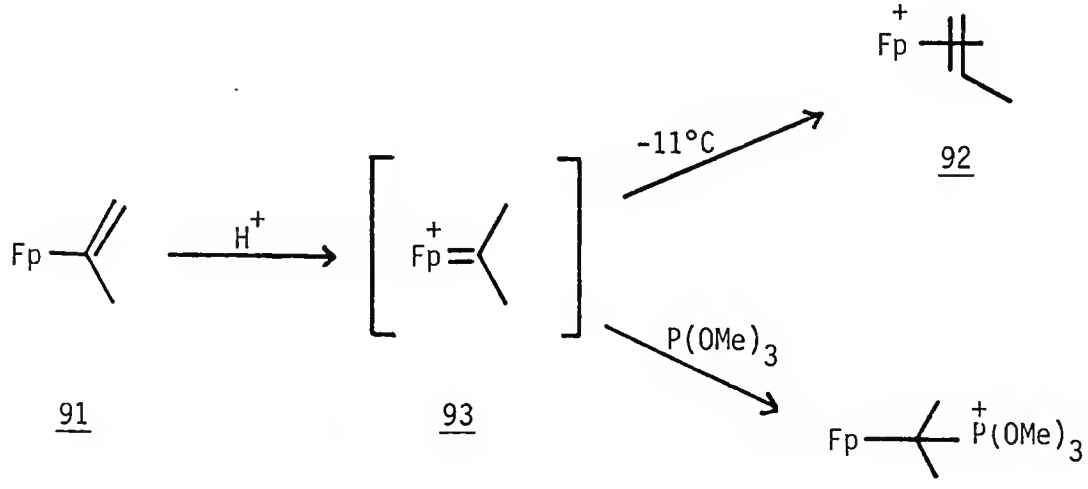
The second proposed reaction is protonation of the methoxy group to give the allyl cation (33) which abstracts a hydride* to generate

* Possible hydride donors include Et_2O, CH_3OH (unlikely) or starting material.

Scheme 2

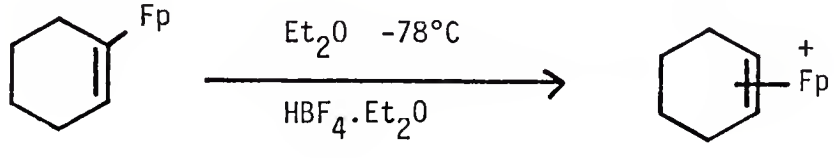

OMe
Fp
72
HBF4
HBF4
OMe
Fp
+
83b
83a
+
Fp
33
H−
Fp
88
OMe
Fp
+
84
NaI
acetone
0
80
+
Fp
Fp
89a
89b
+
Fp
90
NaI
acetone
81

the sigma complex (88). This, in turn, could react with any acid present to give the carbocyclic carbene (89) which should rearrange to the π-complex (90). This is reasonable since Casey and co-workers[43] recently found that treatment of (91) with $HBF_4 \cdot Et_2O$ gave the π-complex



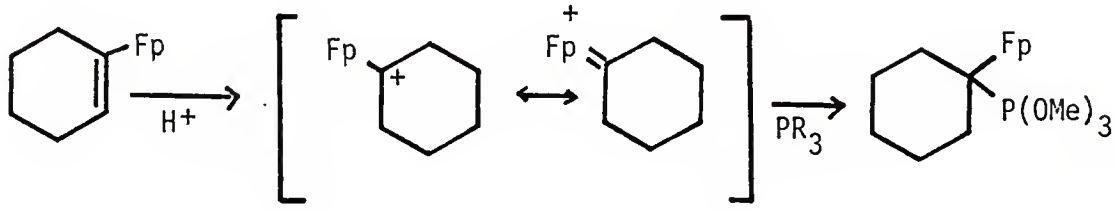
91 93 92 94

(92), via the carbene (93). The latter was trapped with $P(OMe)_3$ to give (94). Further evidence for the proposed conversion of (88) to (90) was obtained by treating the carbocyclic sigma complex (95) with $HBF_4 \cdot Et_2O$,



95 96

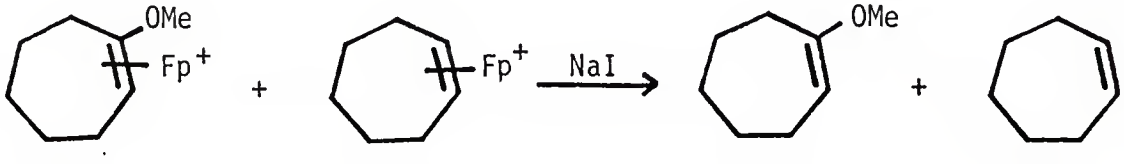
at -78°C, to afford (96) in a 96% yield. Evidence for a carbene intermediate (97) was obtained by protonation of (95) in the presence of $P(OMe)_3$ which led to the isolation of (98). Finally, further proof



95 97 98

for the formation of (90) comes from the fact that the ^1H NMR spectrum (Figure 3) reveals a singlet at δ 5.80 (Cp) which can be overlapped with the known carbocyclic π-complex (90) as seen in Figure 4.

As mentioned above, treatment of (84) and (90) with excess NaI in d_6-acetone should release the corresponding carbocyclic compounds (99) and (81), respectively. Although it seems unlikely



84 90 99 81

that (99) could result from reaction with I^- to generate (80), it is feasible that in the presence of FpI this could be possible. Further proof of this can been seen in

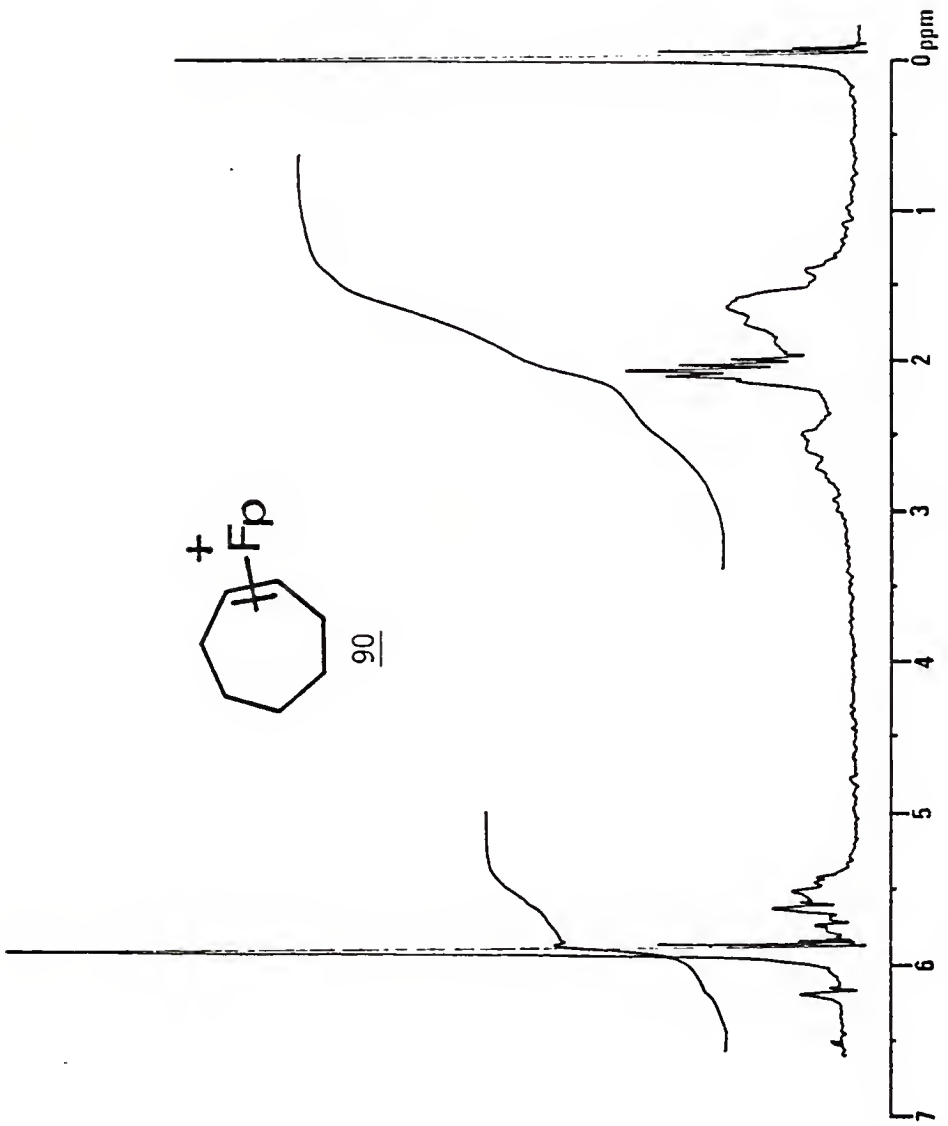
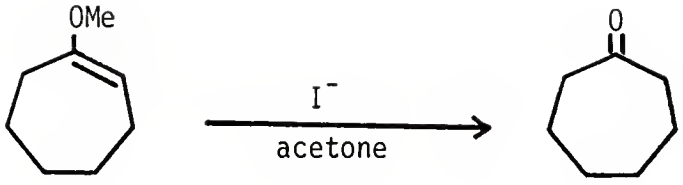
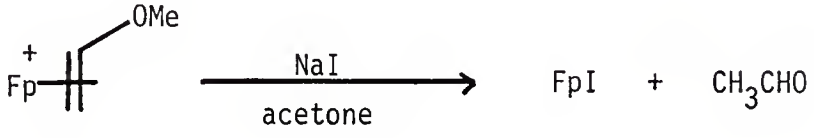


Figure 4. ^{1}H NMR spectrum of (90) in d_6-acetone.



99 80

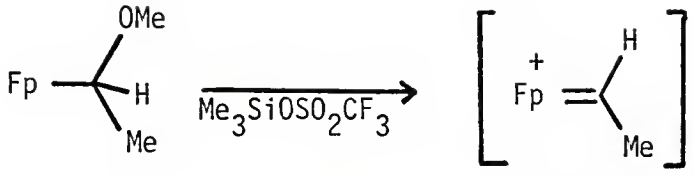
the treatment of the known π-complex (86)[44a] with excess NaI in d_6-acetone to give FpI and acetaldehyde.[44b]



86

Regardless of the mechanism of formation of these products the desired allene complex (35) was not observed although some reaction appeared to be taking place on the double bond. Therefore, a search for a methoxy abstractor which would not react with the double bond was conducted.

Recently Brookhart and Tucker[45] reported that treatment of (100) with trimethylsilyl trifluoromethanesulfone, $Me_3SiOSO_2CF_3$, (101) afforded the carbene complex (102) by simple methoxy abstraction.



100 102

Accordingly, (72) was treated with $Me_3SiOSO_2CF_3$ at -78°C to give an immediate precipitation which when warmed to room temperature followed by removal of the solvent afforded a brownish oil (Figure 5). When excess NaI was added to a d_6-acetone solution of this oil an immediate color change, brown to purple, occurred (Figure 6). Work-up afforded FpI, cycloheptene (81), 1,3-cycloheptadiene (82) and trace amounts of cycloheptanone (80) by GC/MS. A possible mechanism for formation of these products is seen in Scheme 3.

In this scheme addition of $Me_3SiOSO_2CF_3$ gives the allyl cation (33)* which could rearrange to (90) as the solution is warmed as seen in Scheme 2. In a competing reaction (33) could lose H^+ to give (103). This in turn could then react with H^+ to give the more stable carbene

* The Fp may not be able to assist in the loss of the methoxy group because this would force the leaving group into the center of the ring system.

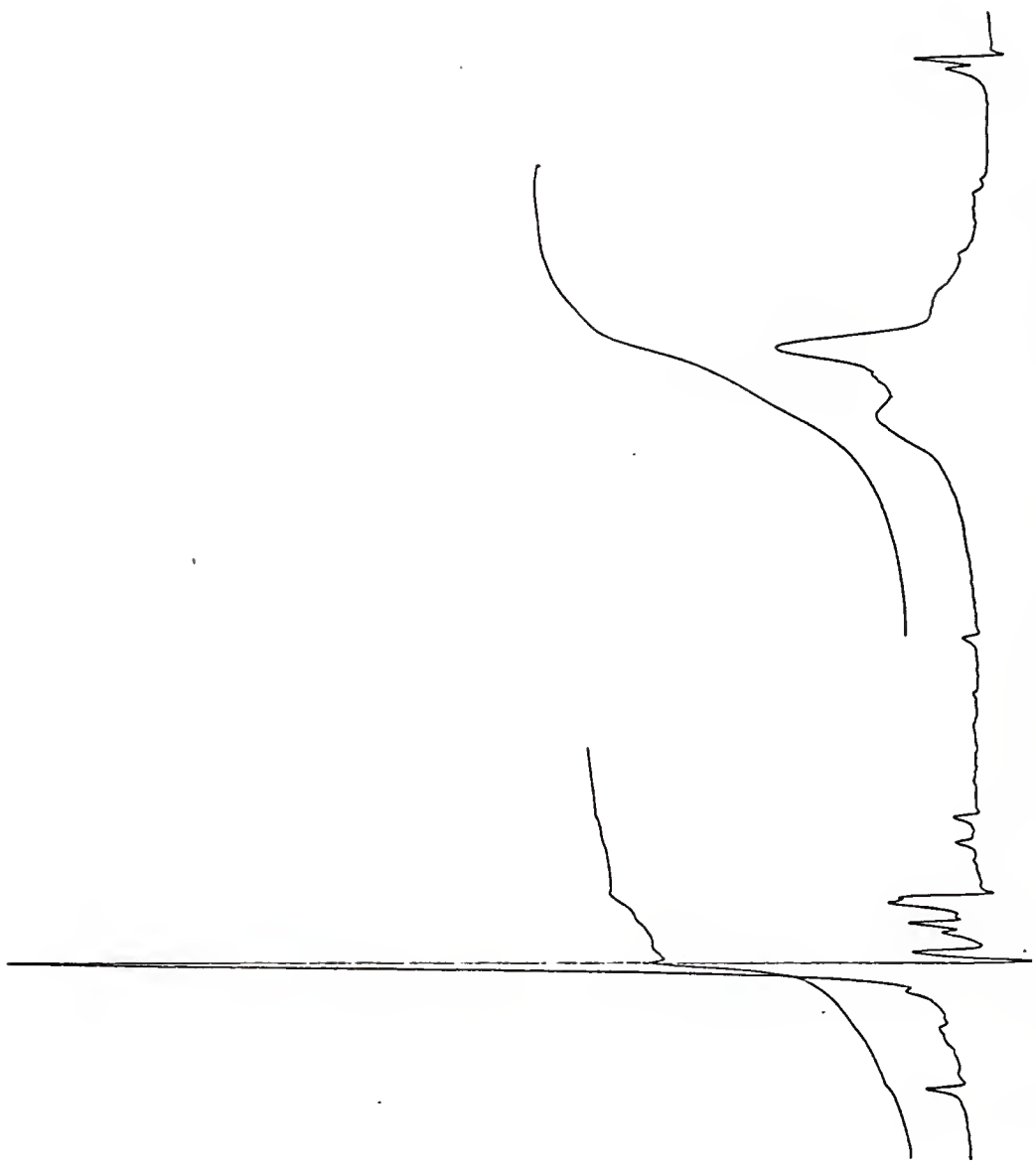


Figure 5. ^{1}H NMR spectrum of the crude products from the addition of $Me_3SiOSO_2CF_3$ to (72).

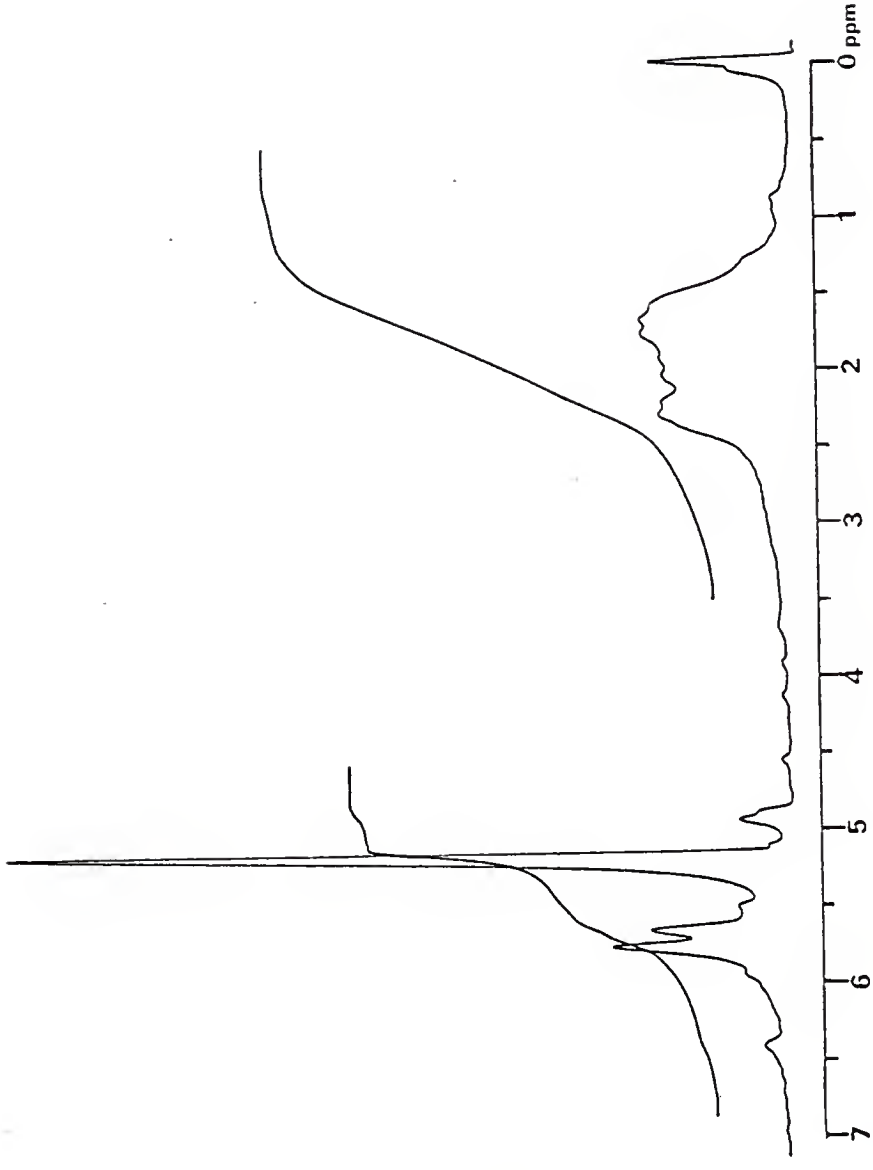
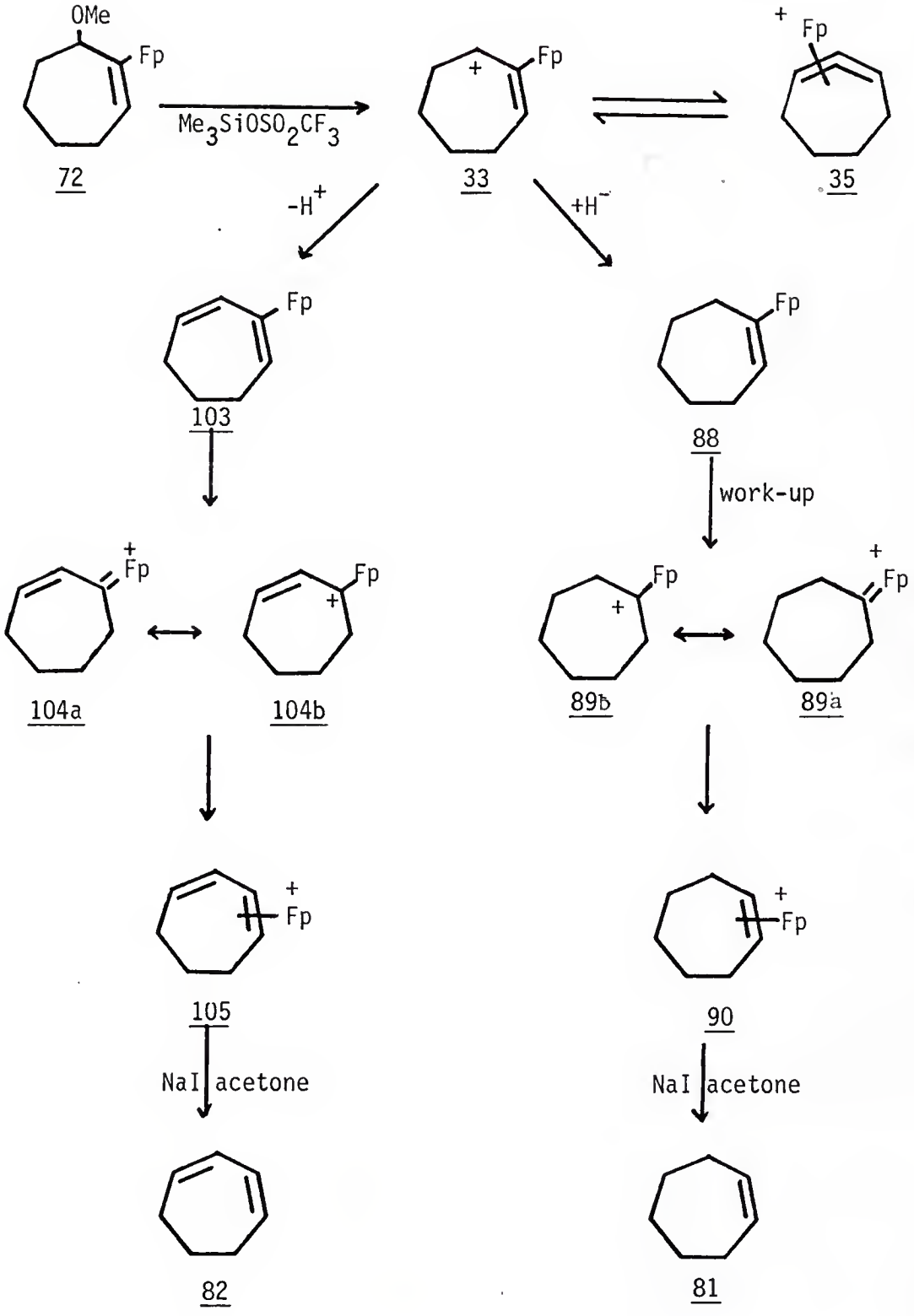


Figure 6. ^{1}H NMR spectrum of the addition of NaI to the crude products of Figure 5.

Scheme 3


OMe
Fp
72
$Me_3SiOSO_2CF_3$
33
35
$-H^+$
$+H^-$
103
88
work-up
104a
104b
89b
89a
105
90
NaI acetone
NaI acetone
82
81

complex (104) followed by rearrangement to give (105). Here again reaction of (90) and (105) with NaI should give FpI, cycloheptene (81) and 1,3-cycloheptadiene (82), as observed.

Since the treatment of (72) with $Me_3SiOSO_2CF_3$ did not give rise to any cycloheptanone (80) or any organic compounds with oxygen present, it appears that indeed the methoxy was clearly abstracted. The crucial questions are whether the precursor to (90) and (105) is the allyl cation (33) or the allene complex (35) and the structure of the precipitate initially formed. To address the latter, we undertook a low temperature ^1H NMR study of this material.

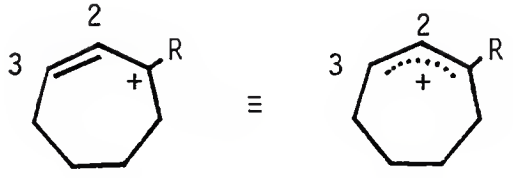
To prepare for this study, a search for suitable models revealed that Olah and Liang[46] had reported the preparation and properties of (106a-c) in superacid. It was found that in the ^1H NMR spectrum, the

106(a-c) R: a=H b=CH_3 c=Cl

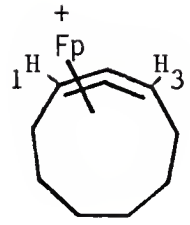
parent cation (106a) showed a doublet at 10.18 ppm (H_1 + H_3) and a triplet at 8.34 (H_2). Substituted allyl cations show vinyl resonances slightly upfield from these values as seen in Table 4.

Foxman and co-workers[22] reported the synthesis of (23) as a stable crystalline solid whose ^1H NMR revealed resonance at 4.45 ppm (H_1), 6.50 (H_3) and 5.80 (Cp), which we used as a model for the allene complex (35).

Table 4. ^{1}H NMR resonances for (106a-c)

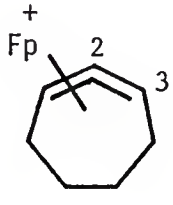


R	H_1	H_2	H_3
a) H	δ 10.18	δ 8.34	δ 10.18
b) Me	-	δ 8.05	δ 9.50
c) Cl	-	δ 8.05	δ 9.58

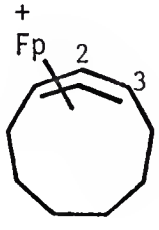


23

From these models clearly the carbocyclic allene complex (35) or the carbocyclic allyl cation (33) should have very different and characteristic ^1H NMR spectra which should make it easy to distinguish between them. A CD_2Cl_2 solution of the methoxy complex (72) was treated with a slight excess of $Me_3SiOSO_2CF_3$ at -78°C in an NMR tube and the ^1H NMR spectrum recorded. This revealed* a singlet at 5.70 ppm (Cp) and two multiplets at 6.50 (H_3) and 4.2 (H_1) (Figure 7) which corresponds



35



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* No resonances were observed from 7 to 15 ppm and 0 to -13 ppm.

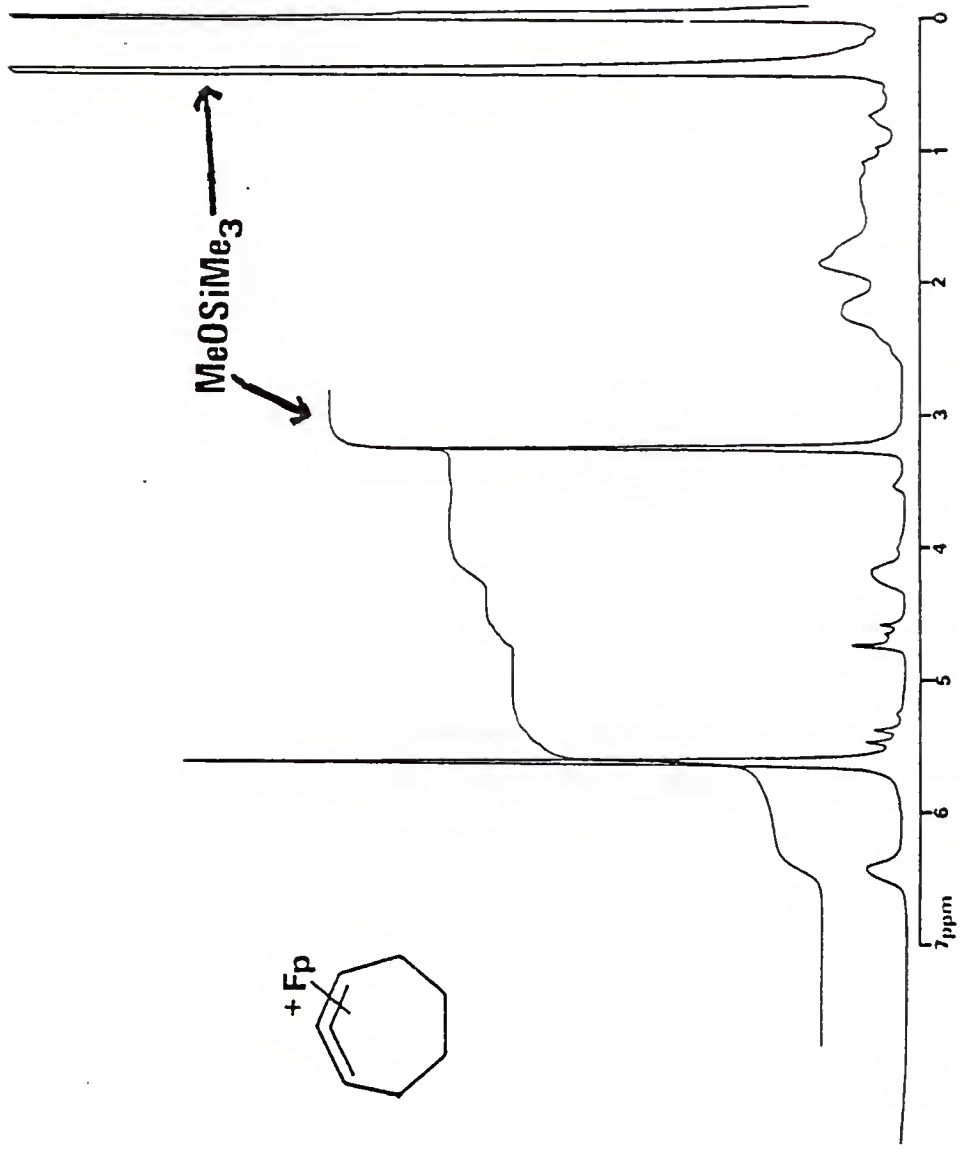
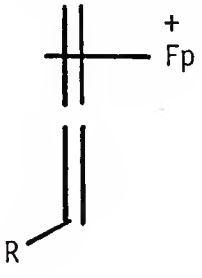


Figure 7. 100 MHz ^1H NMR spectrum of the crude products from the addition of $Me_3SiOSO_2CF_3$ to (72) in CD_2Cl_2 at -30°C.

closely with (23) (Figure 8) as reported by Foxman and co-workers.[22] Further evidence for the allene structure (35) would be the observation of fluxional behavior[22,47] as the temperature is changed. And indeed, as the sample was slowly warmed from 0°C* to 40°C, a coalescence of the multiplets at 6.5 ppm (H_3) and 4.2 ppm (H_1) was observed (Figure 9) occurring somewhere between 20° and 40°C. After the sample was warmed to 40°C, it could be cooled back to 0°C to reveal the multiplets at 6.5 ppm and 4.2 again. As expected from earlier work, if the sample is kept at room temperature in solution it slowly decomposes.

A characteristic property of Fp acyclic allene complexes is their reactions with nucleophiles such as alcohols. We therefore decided to examine the reaction of (35) with ethanol. Interest in nucleophilic reactions with acyclic Fp allenes ran rather high about 10 years ago. Lichtenberg and Wojcicki[48] reported that treatment of (107) with most



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* (35) Is stable for at least two hours at 0°C.

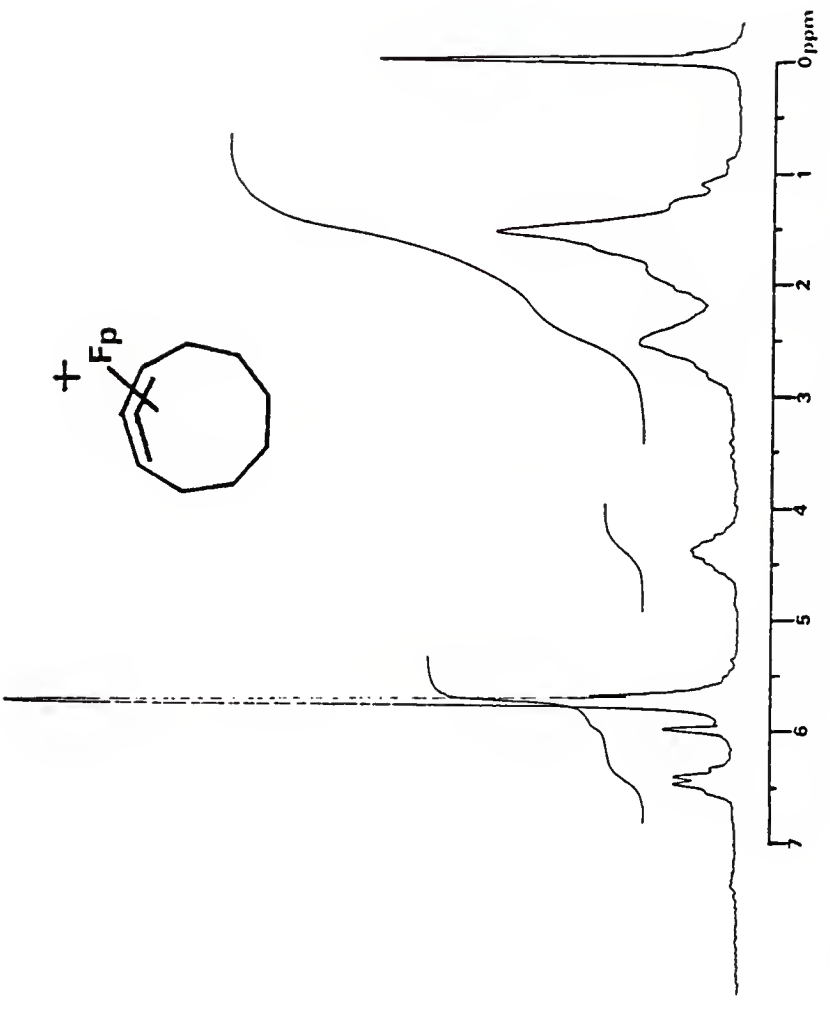


Figure 8. ^{1}H NMR spectrum of (23) in CD_3NO_2 at room temperature.

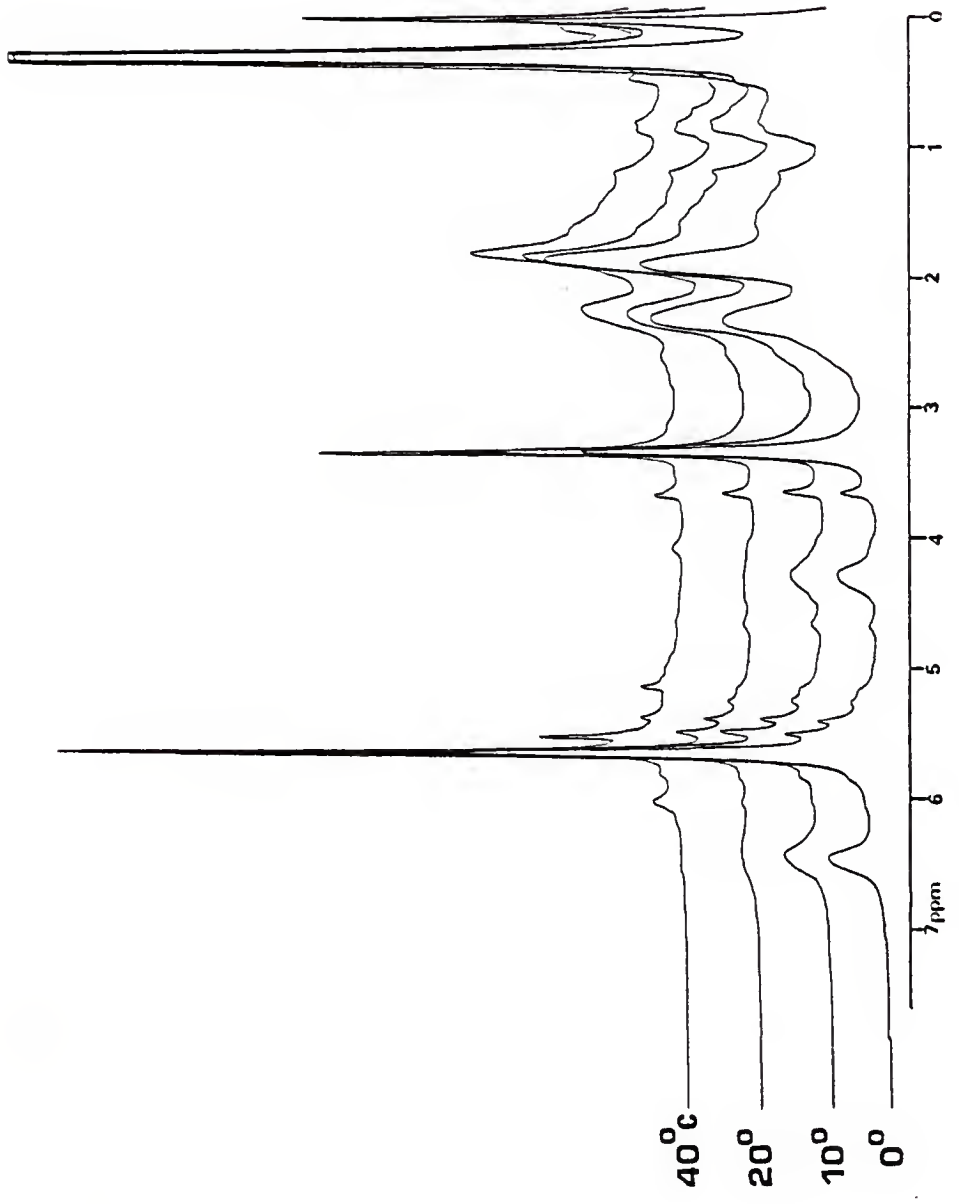
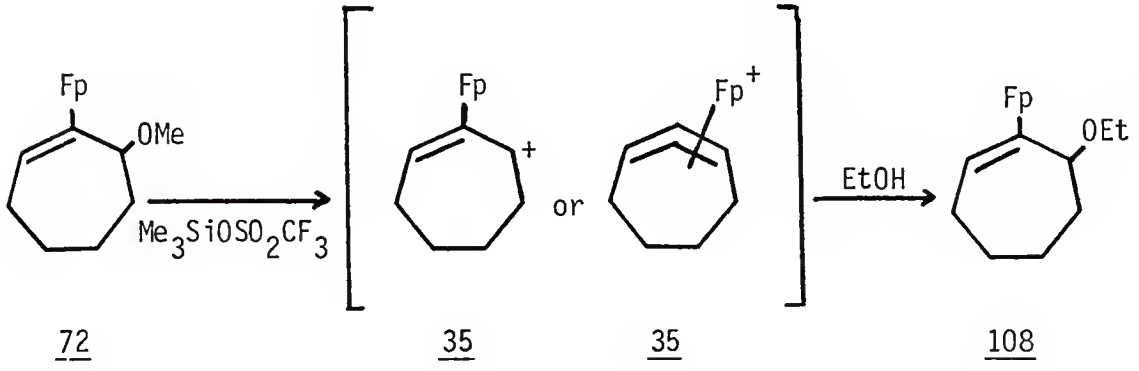


Figure 9. 100 MHz ^{1}H NMR spectra displaying the fluxional behavor of (35).

nucleophiles* afforded attack at the terminal carbon with migration of the metal to the central carbon. One exception was MeO^- which preferentially or exclusively attacks at the central carbon (Figure 10).

We found that the reaction of (72) was $Me_3SiOSO_2CF_3$ at -78°C followed by the addition of a cold (0°C) mixture of $EtOH/Na_2CO_3$‡ afforded (108)† in a 54% yield. To prove the structure assigned to (108) an alternate synthesis was accomplished as seen in Scheme 4.



72 35 35 108

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* Non complexed allenes are inert to attack by nucleophiles.

‡ Addition of the alcohol either two minutes or 2.5 hours after the initial addition gave the same product.

† This result is not only consistent with addition to the allene complex but possibly to the allyl cation complex too.

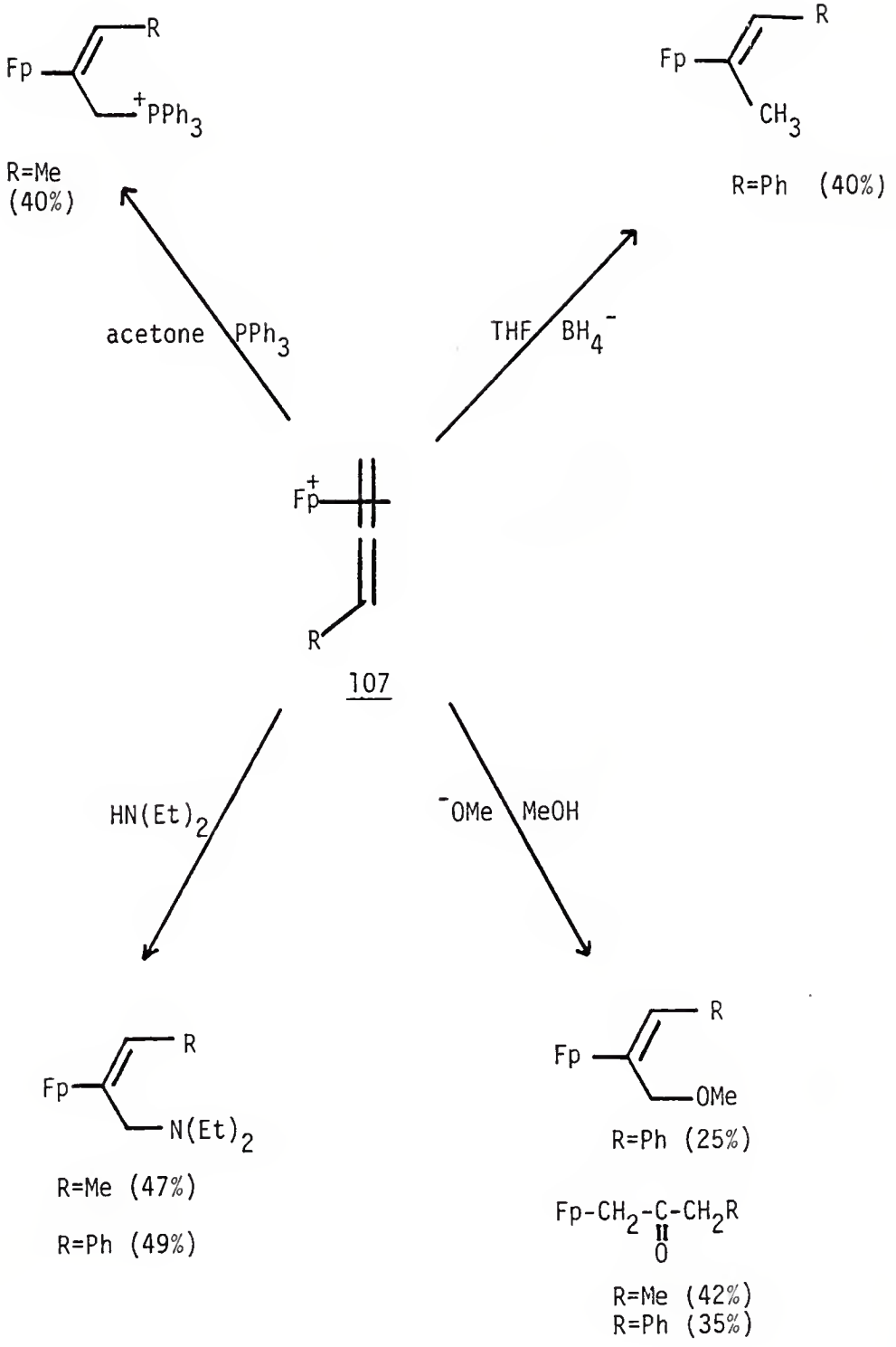
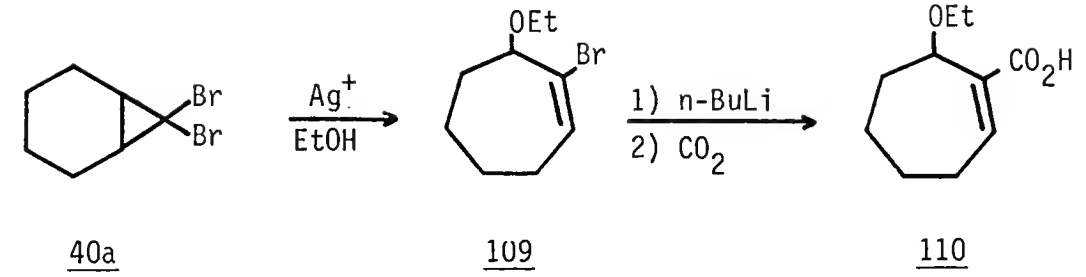
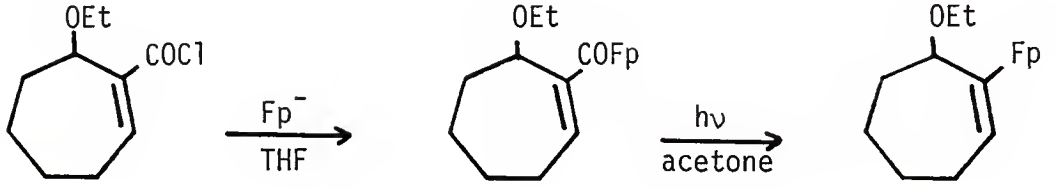


Figure 10. The addition of Nu^- to (107).

Scheme 4



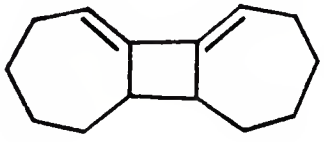
40a 109 110



111 112 108

In this sequence, treatment of (40a) with $AgNO_3$ in EtOH gave (109) in a 75% yield. Treatment of (109) with n-BuLi at -78°C followed by addition of CO_2 and acid work-up gave (110) in a 65% yield. To the acid (110) was added $SOCl_2$ in benzene to give the acid chloride (111). Addition of the acid chloride (111) to a suspension of Fp anion in THF at -78°C gave the desired acyl complex (112). The acyl complex (112) was photolyzed for 2 hours at 0°C in acetone to give (108) as a brownish, air-sensitive oil, 28% from the acid chloride. The ^1H NMR spectrum of (108) is given in Figure 11, which is identical with that obtained from the allene complex.

Up to this point, evidence for the carbocyclic allene structure (35) has been based on the crude ^1H NMR, the observation of its fluxional behavior and its reaction with EtOH. It would be desirable to release the allene ligand and detect it as its dimer (113). A solution



113

of (72) in CD_2Cl_2 was therefore treated with $Me_3SiOSO_2CF_3$ followed by the addition of $Me_4N^+I^-$, which is soluble in CH_2Cl_2. Although FpI was formed the dimer (113) was not observed.

On searching the literature it was found that this result is not inconsistent with the allene structure because Lichtenberg and Wojcicki[49] found that treatment of (107) with $^+NR_4I^-$ gave FpI as the

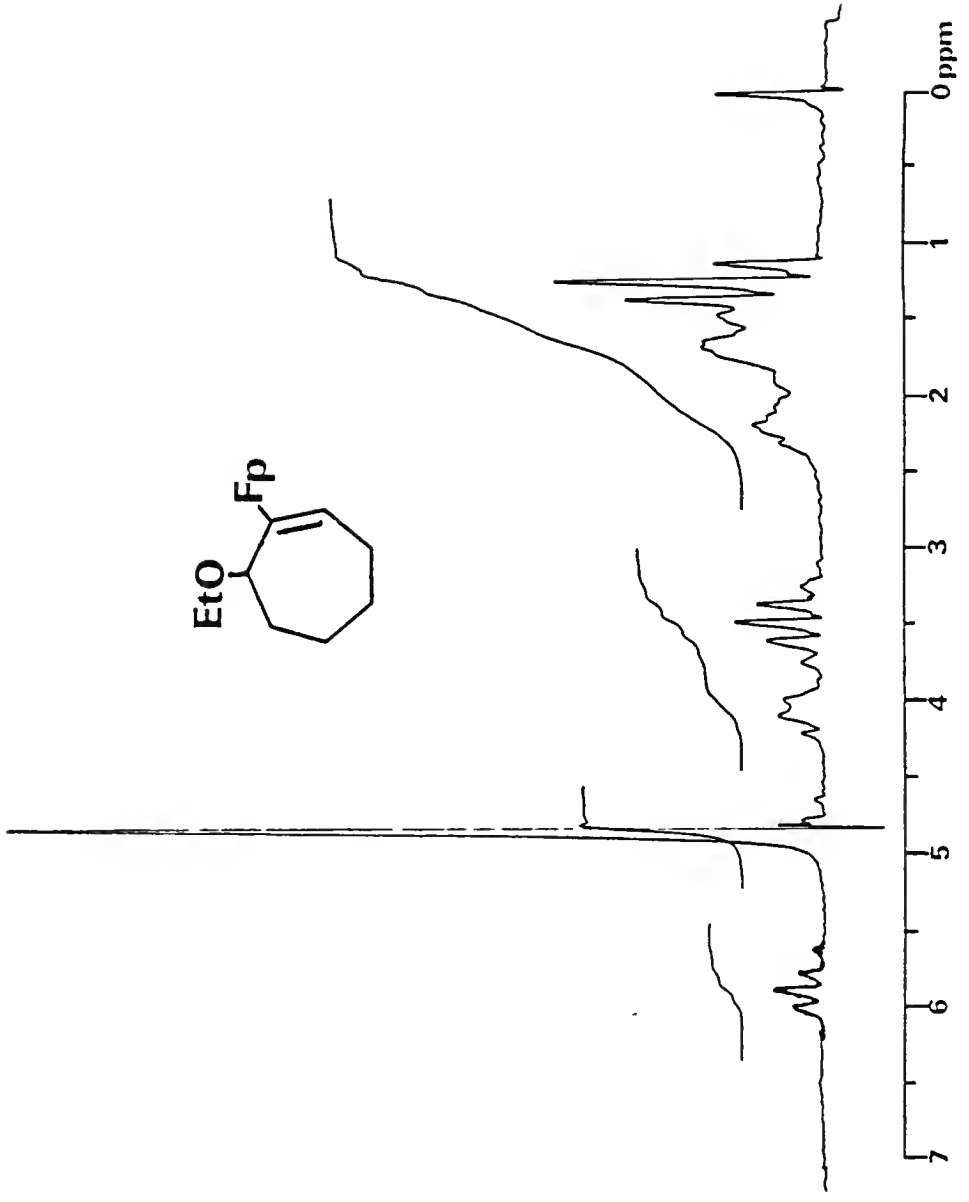
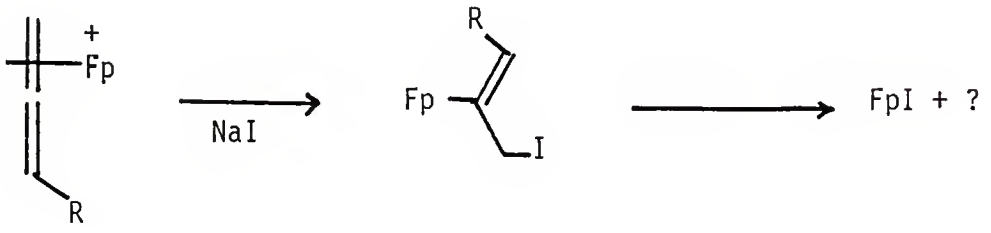


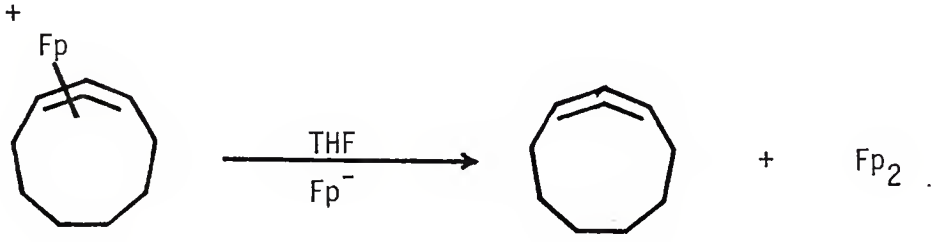
Figure 11. ^{1}H NMR spectrum of (108) in $CDCl_3$.

major product; however no free allene was observed. An unstable material (114) was characterized by IR which was believed to



107 114

spontaneously decompose* to FpI and a tarrish material at room temperature. It has also been reported that (14) was released from (23) with Fp anion.[22] We therefore treated (35) with Fp anion in THF at -78°C but again no trace of the dimer (113) could be detected even though Fp_2 was isolated.



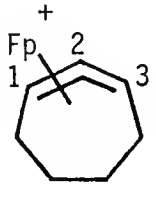
23 14

* A similar decomposition has been noted by Lukas and co-workers[50] for a Pt complex.

Since our attempts to release the carbocyclic allene were unsuccessful, an attempt to isolate and further characterize the carbocyclic allene complex (35) was next approached.

One of the major problems isolating (35) was its instability in solution at room temperature; however, if the solution was kept at 0°C the allene complex seemed to be somewhat stable for at least two hours. Therefore, after the initial generation of (35) at -78°C the reaction mixture was warmed to 0°C at which time the solvent was removed in vacuo. This afforded a tan solid (71%) which gave the ^{1}H NMR spectrum shown in Figure 12. This material,which is believed to be the allene complex (35), appears to be stable indefinitely in the solid phase at -78°C under a N_2 atmosphere; in fact it was sufficiently stable to obtain a correct C,H analysis.

To further prove that indeed the new complex (35) had the allene structure a ^{13}C NMR spectrum (Figure 13) was taken at -20°C. In this spectrum the resonance for the allene carbons C_1-C_3 appeared at 150 ppm (C_2), 125.8 (C_3) and 43.6 (C_1). These compare quite well with the resonances for the 1,2-cyclononadiene complex (23) which shows similar resonances for carbons (C_1-C_3) at 148.5 ppm (C_2), 122.3 (C_3) and 51.3 (C_1) as seen in Figure 14. This is strong evidence for the structural similarity of complex (23) and (35).



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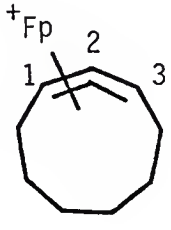

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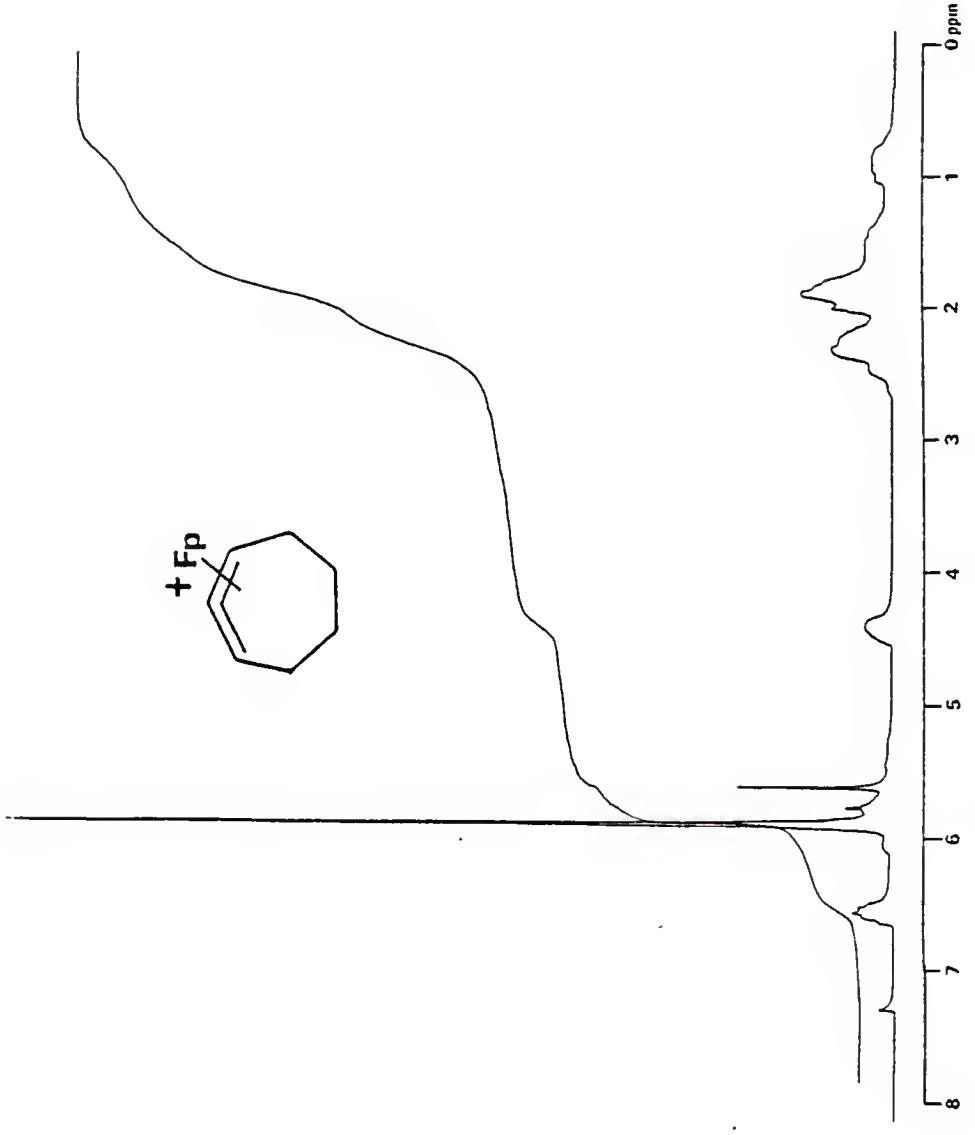


Figure 12. 100 MHz ^{1}H NMR spectrum of (35) in d_6-acetone at -20°C.

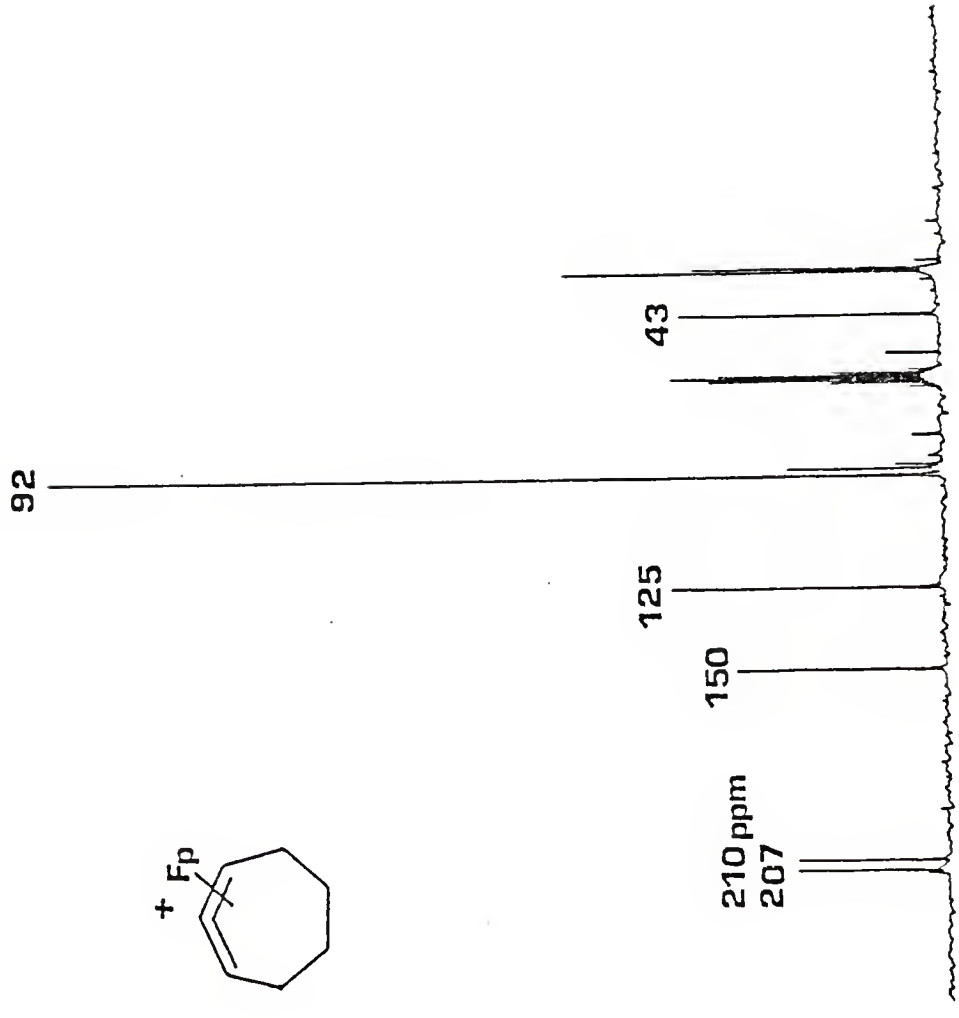


Figure 13. ^{13}C NMR spectrum of (35) in CD_3NO_2 at -20°C.

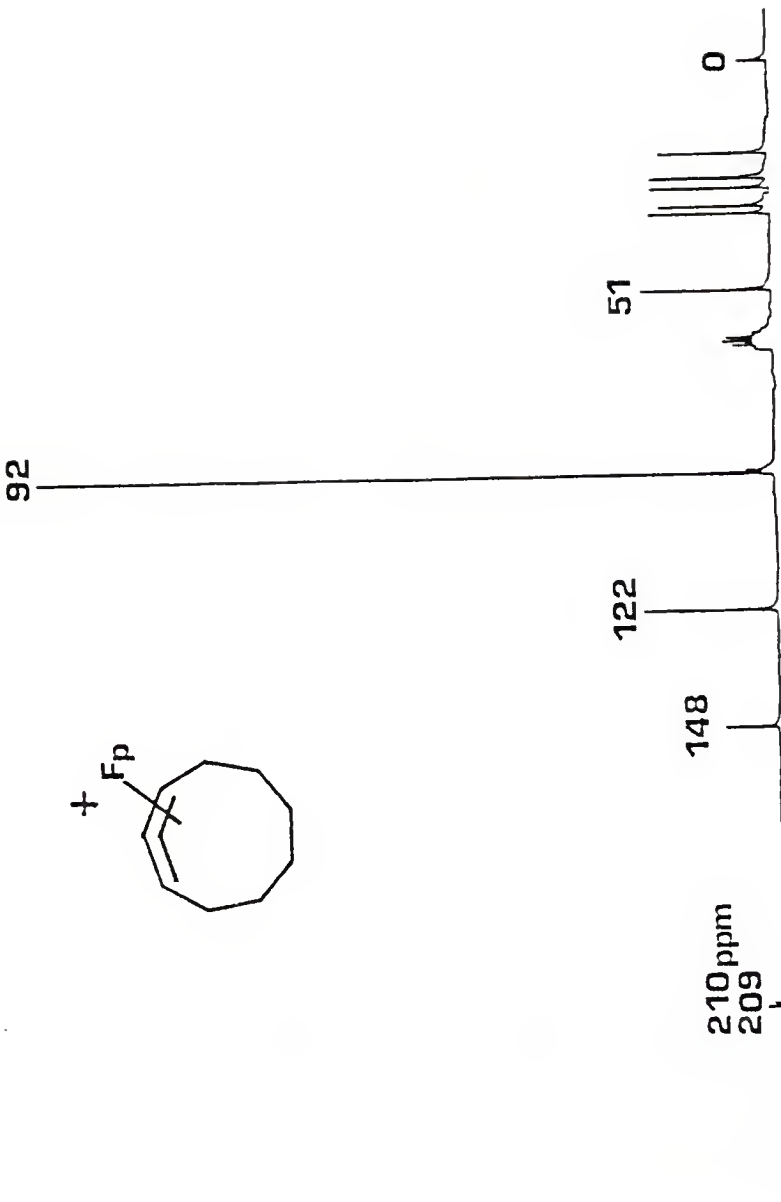
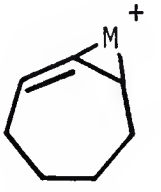


Figure 14. ^{13}C NMR spectrum of (23) in CD_3NO_2 at room temperature.

In both cases the upfield shift of the C_1 and C_2 carbons as compared with uncomplexed allenes suggests significant metallocyclopropyl character as depicted in (115) and (116). Furthermore, in

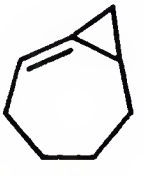
115

+



116

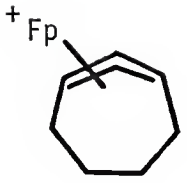
(35) the C_1 resonance is ca. 8 ppm upfield from the C_1 resonance in (23) which indicates slightly more cyclopropyl character. This is not surprising since the geometrical constraints opposing incorporation of the cyclopropyl ring in a structure such as (118) are less



118

16

than for a double bond as in (16). This relief of strain can be seen best in the fact that (118)[12,51,52] can be isolated whereas the more strained allene (16) has been generated at low temperatures, but has not been observed as the free molecule.[17]



35

At this point since the pure carbocyclic allene complex (35) was in hand a more detailed examination of its fluxional behavior was attempted. As discussed earlier the low temperature, at -39°C, ^{1}H NMR spectrum of (35) exhibits two multiplets at 6.55 ppm (Ha) and 4.45 (Hb). As the temperature was raised the point of coalescence was observed at 29°C as seen in Figure 15. Here exchange of Ha and Hb became rapid on the NMR time scale. Using Equation 1,[53] the free energy of activation ($\Delta G^{\ddagger}$) was obtained. In this equation, Tc represents the

$$\Delta G^{\ddagger} = R\ Tc(\log_e Tc/\delta\nu + 22.96)$$

Equation 1

temperature of coalescence and $\delta\nu$ is the distance between Hb and Ha in Hz. The barrier for interconversion of isomeric allene complexes (35a $\rightleftarrows$ 35b) was calculated to be 13.9 ± 0.2 kcal/mole with $\delta\nu$ equal to 215.6 Hz at -78°C. This result corresponds to the activation barrier

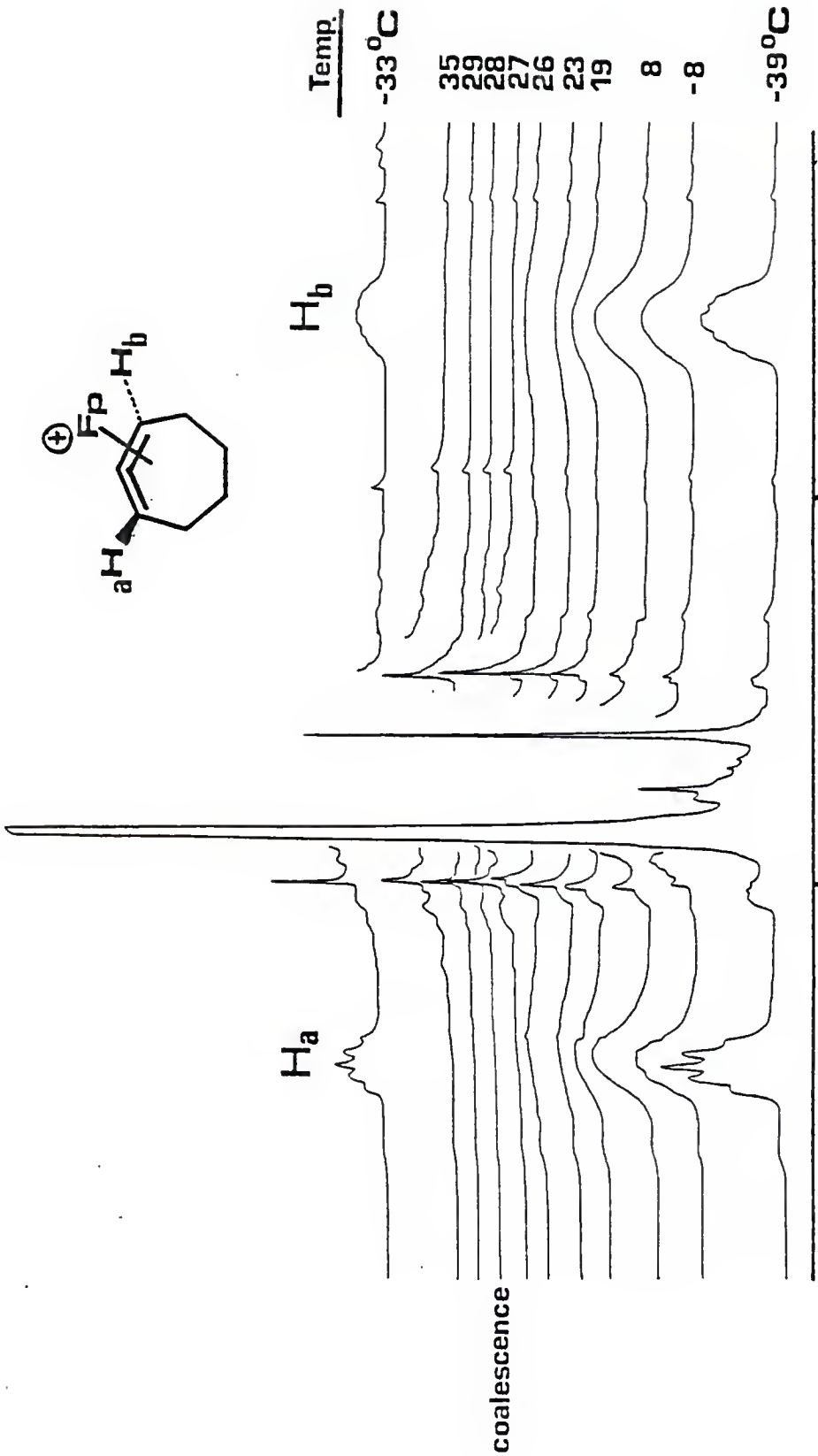
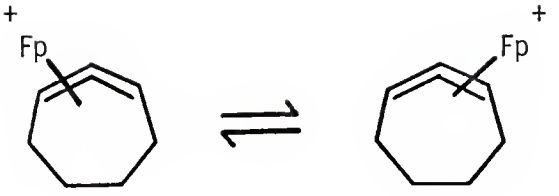
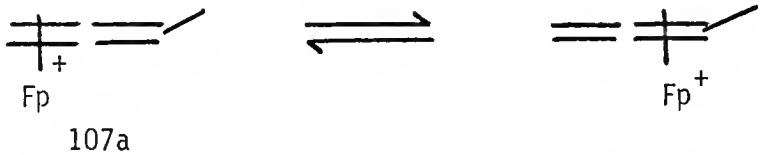


Figure 15. 100 MHz ^1H NMR spectra of (35) in d_6-acetone.

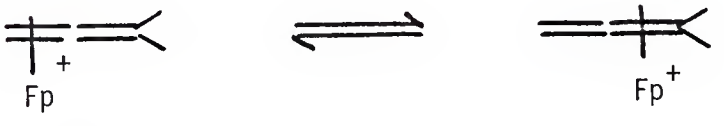


35a 35b

of known acyclic allenes[22] of 23.1, 18.0 and 16.3 kcal/mole for (107a), (119) and (120), respectively.



107a



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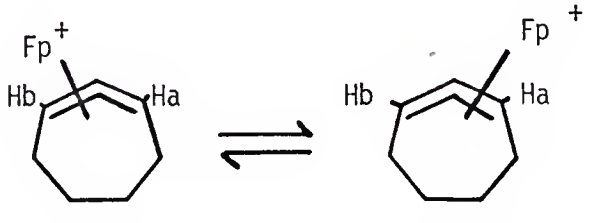
120

Further support for the structure of (35) comes from an extremely useful NMR technique known as spin saturation transfer,[54-57] an NMR



35a 35b

technique which can be applied to systems that are in rapid equilibrium. Since Ha and Hb have different chemical shifts (δ 6.50 and 4.45, respectively; Figure 12) then either Ha or Hb could be specifically saturated by applying a strong rf field at the appropriate frequency. If the exchange rate between Ha and Hb is comparable to the relaxation rate at both sites, then complete saturation of one resonance will result in partial or complete saturation of the other resonance. If the exchange process becomes sufficiently slow at low temperatures, then saturation at Hb (or Ha) should result in no apparent saturation of Ha (or Hb) since the relaxation process should take place before exchange occurs. Conversely, if the exchange process is rapid at higher temperatures then saturation of Hb should result in partial or complete saturation of Ha since the relaxation process does not take place before exchange occurs.

Accordingly, the ^{1}H NMR spectrum of (35) reveals a multiplet at δ 6.55 (Ha) and 4.45 (Hb) as seen in Figure 16a. When a strong rf field was applied at Ha (δ 6.55 at -20°C) the exchange process between Hb and Ha apparently takes place without relaxation occurring in the transfer process (Figure 16b) because the intensity of Hb was observed to decrease. However, at -60°C the exchange process is significantly slower than relaxation so complete relaxation occurs before exchange, Hb to Ha. As a result, the intensity of Hb did not diminish when Ha was saturated. At -40°C, saturation of Ha results in partial saturation of Hb (Figure 17b) thus resulting in an exchange process somewhat slower than that at -20°C (Figure 16b) but faster than the exchange at -60°C (Figure 17c). This is feasible for (35) since one would expect at high temperatures (in this case -20°C) a fast [1,2]Fp shift allowing Ha and Hb to exchange

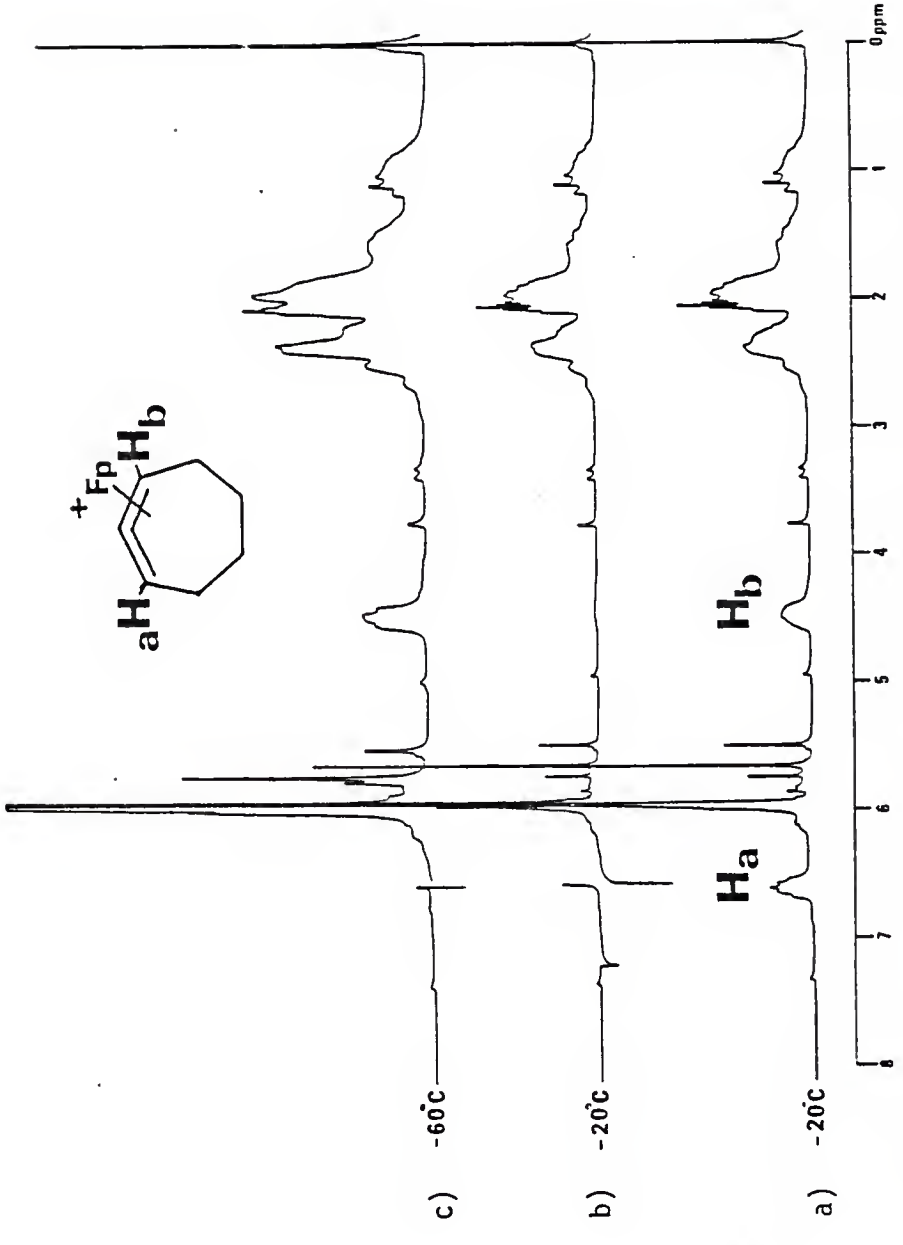


Figure 16. (a) 100 MHz ^{1}H NMR spectra of (35) in d_6-acetone; (b) irradiation of Ha at -20°C; (c) irradiation of Ha at -60°C.

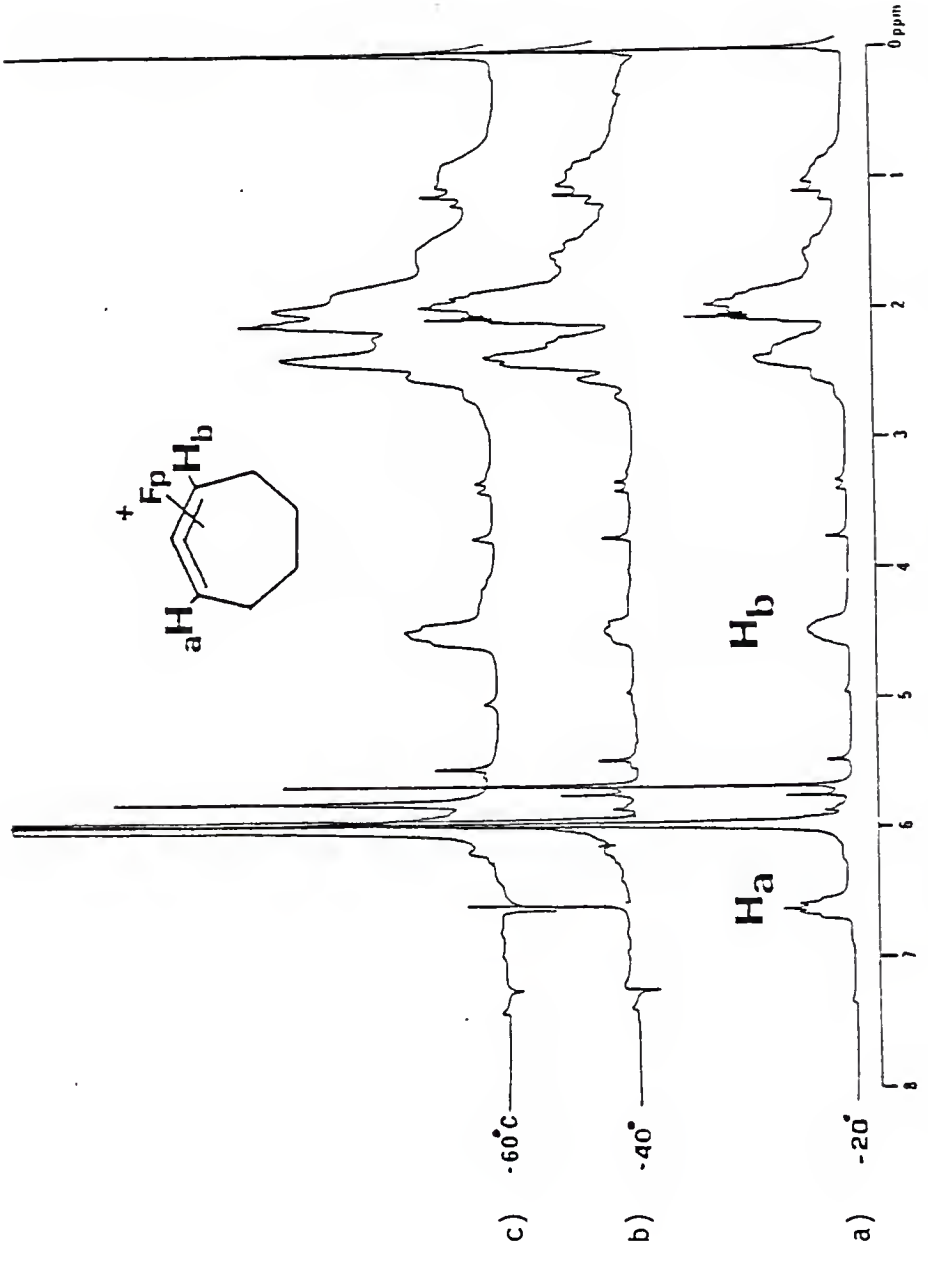


Figure 17. (a) 100 MHz ^{1}H NMR spectra of (35) in d_6-acetone; (b) irradiation of Ha at -40°C; (c) irradiation of ^{6}Ha at -60°C.

whereas at lower temperatures the exchange is slowed down so that the exchange between Hb and Ha is shown according to the NMR time scale.

At this point, we decided to reexamine some unanswered questions. As mentioned before, addition of NaI to a crude reaction mixture of (35) did not give the dimer (113) although FpI was generated. Since the allene complex (35) could now be obtained as a pure solid we decided to reexamine this reaction.

A sample of the solid allene complex (35) was dissolved in a solution of NaI in d_6-acetone at -78°C. This mixture was then allowed to stir for 2 hours at -78°C followed by 4 hours at room temperature. An examination of the ^1H NMR spectrum (Figure 18) again revealed the presence of FpI. A closer examination of Figure 18 also reveals the presence of cycloheptene (81) and cycloheptadiene (82). Analysis of the mixture showed the amounts of (81) and (82) to be 20% and 49%, respectively. From this result we conclude that the complex rearranges to the corresponding π-complexes (90) and (105) faster than the allene is released. The π-complexes then immediately react with NaI to give the observed olefins (81) and (82).

In an attempt to determine if the precursor to the observed π-complexes (90) and (105) is the allyl cation (33), we decided to see if the addition of Ph_3CH, a good hydride donor, would change the relative amounts of (81) and (83). An excess amount of Ph_3CH was therefore added to a solution of (35) in CH_2Cl_2 at -78°C followed by warming for 3 hours at room temperature. This gave a brownish oil after the removal of the solvent in vacuo. The ^1H NMR spectrum of this oil is seen in Figure 19. Addition of NaI (Figure 20) followed by work-up gave FpI, cycloheptene (34%) and cycloheptadiene (51%). Decomposition under identical

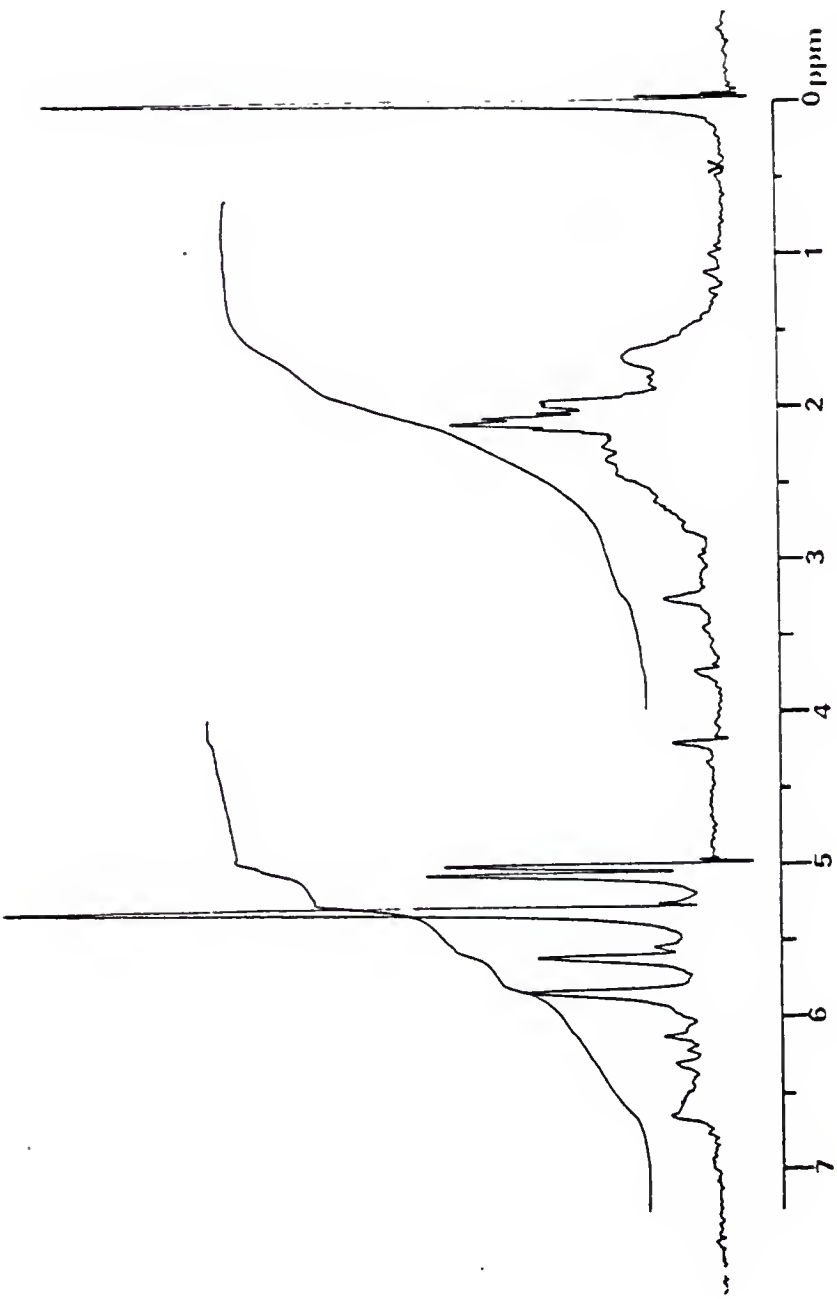


Figure 18. ^{1}H NMR spectrum of (35) and NaI in d_6-acetone at room temperature.

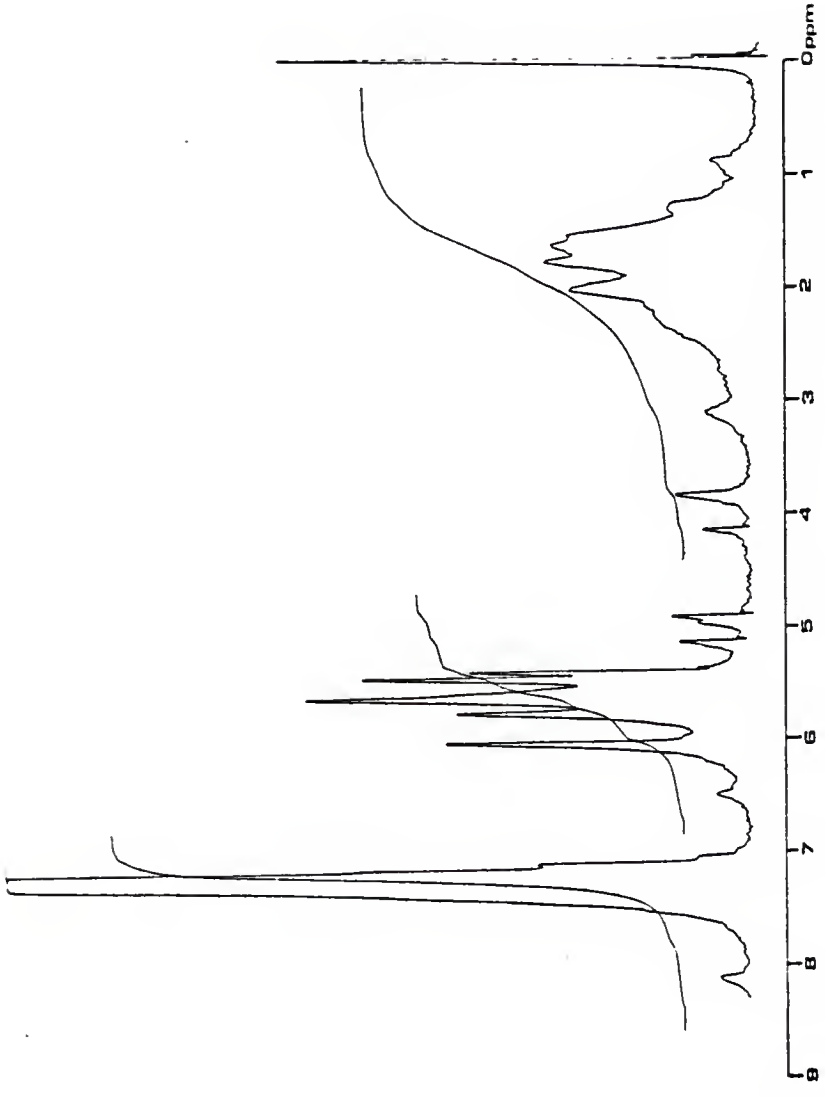


Figure 19. ^1H NMR spectrum of the crude products from the addition of Ph_3CH to (35) in d_6-acetone.

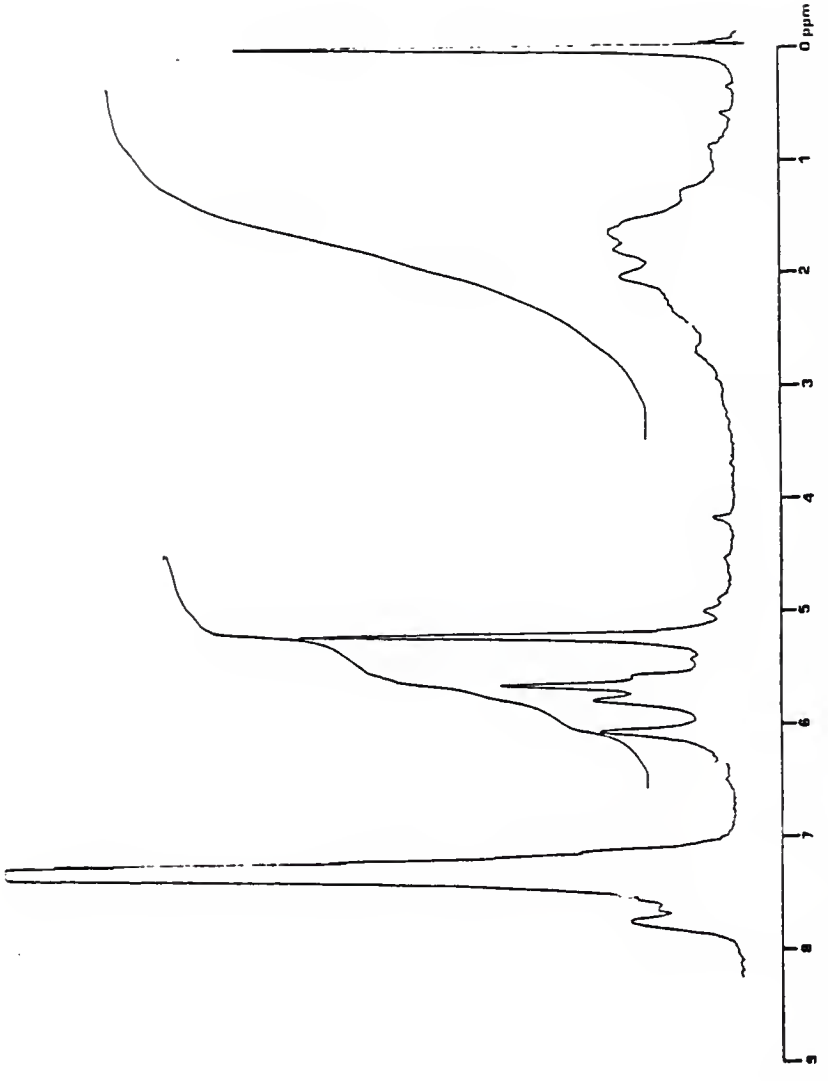


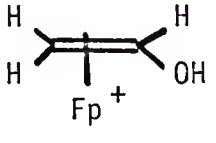
Figure 20. ^{1}H NMR spectrum of the addition of NaI to the products in Figure 19.

conditions in the absence of Ph_3CH gave 1,3-cycloheptadiene (40%) and a trace amount of cycloheptene, from this it appears that the presence of a hydride donor increases the yield of cycloheptene (81) suggesting that indeed the cycloheptene originates from a hydride abstraction reaction.

The stability of the allene complex (35) is also of some importance. While it was found that the complex (35) is stable under a N_2 atmosphere as a solid at -78°C for at least 6 weeks, exposure to the air at ambient temperatures for 30 minutes affords a brownish oil. The ^1H NMR spectrum (Figure 21) of this oil in d_6-acetone reveals a new Cp resonance at 5.7 ppm. Furthermore, addition of NaI to this solution followed by work-up afforded FpI, 83% of cycloheptanone (80) and trace amounts of cycloheptene (81) and 1,3-cycloheptadiene (82) by GC/MS.

One possible mechanism to rationalize this product is shown in Scheme 5.

In this scheme the allene complex (35) reacts with H_2O in the air to afford the sigma complex (121) which can further react with H^+ to generate the carbocyclic carbene (122). This could then rearrange to give the π-complex (123). Although formation of π-complexes of vinyl alcohols[58-60] are known, i.e. (124), it has not been reported whether



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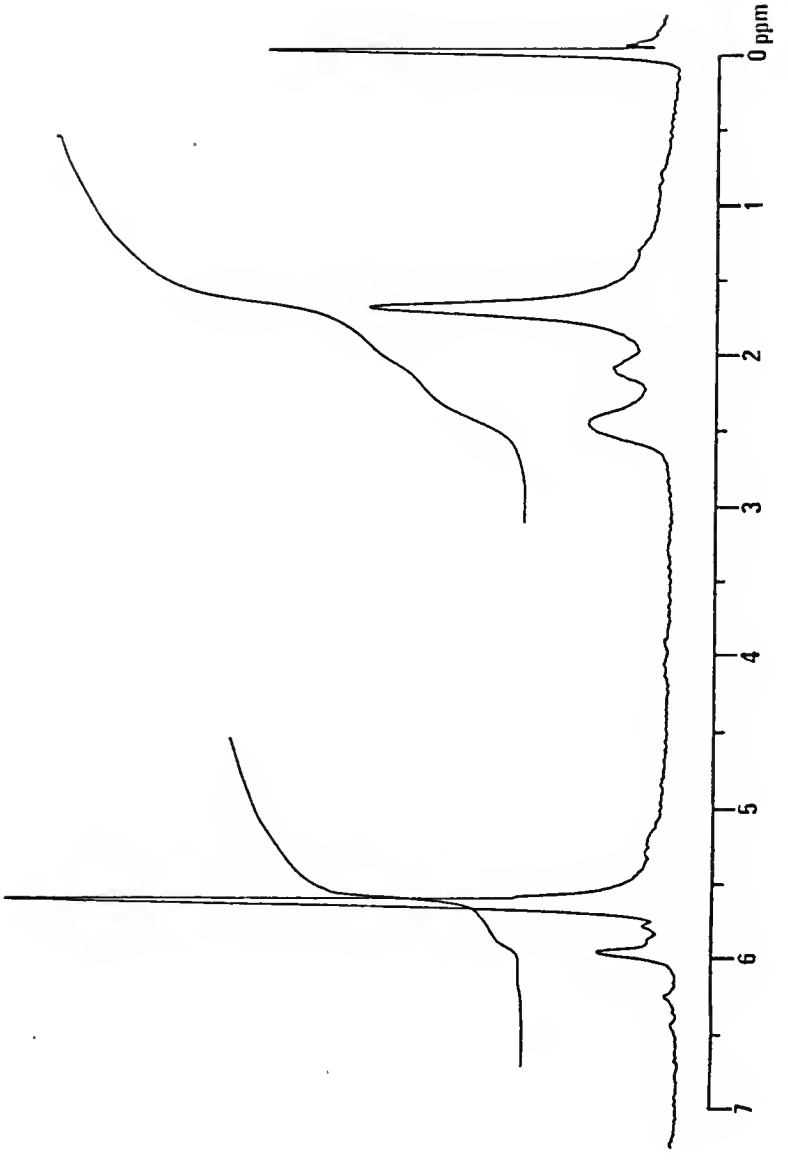
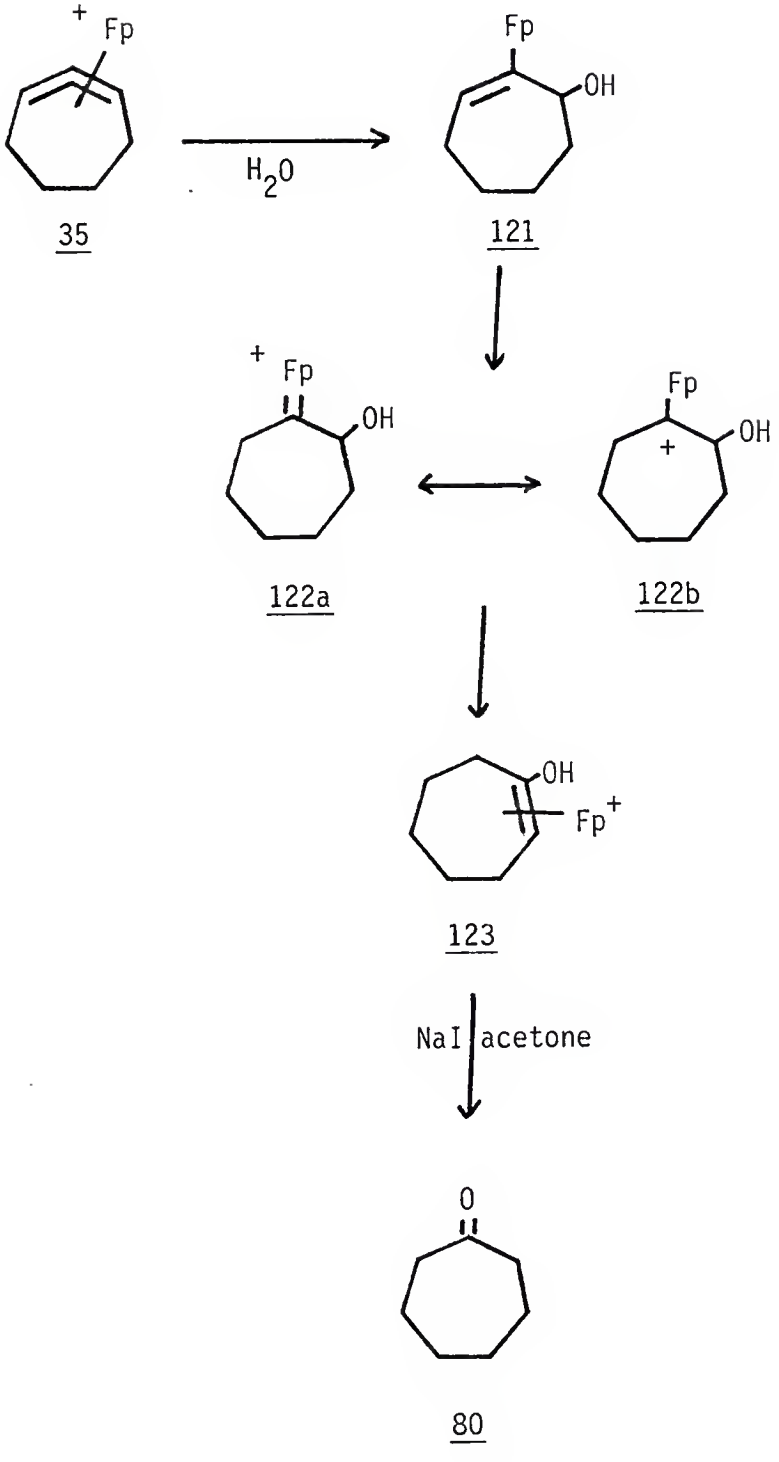


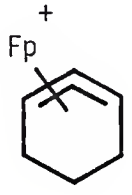
Figure 21. ^{1}H NMR spectrum of the crude products from the exposure of (35) to the air.

Scheme 5


+
Fp
H_2O
Fp
OH
35
121
+
Fp
OH
Fp
OH
+
122a
122b
OH
Fp^+
123
NaI
acetone
O
80

or not NaI would release the π-complex to give the aldehyde or ketone. Since the vinyl ether complex (86) is released by I^- one would expect the same to occur here.

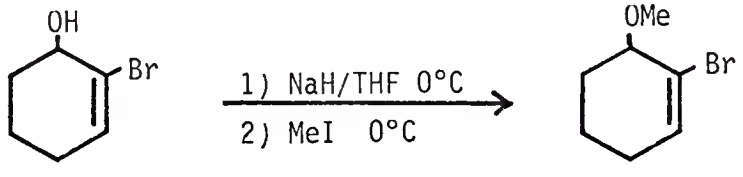
Since it is clear that the carbocyclic allene complex (35) has been generated we decided to explore whether or not the carbocyclic allene complex (125) could be prepared. Therefore, the synthesis of the



125

sigma complex (126) was undertaken. The approach here is similar to the approach used in the synthesis of (72) and is shown in Scheme 6.

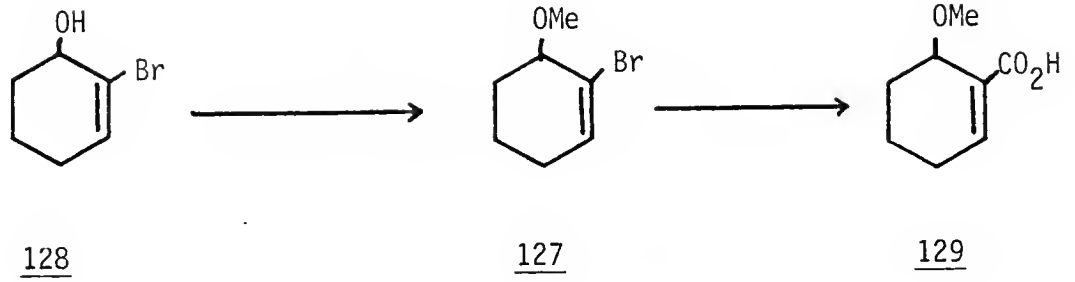
6-Methoxy-1-bromocyclohexene (127) was prepared by the treatment



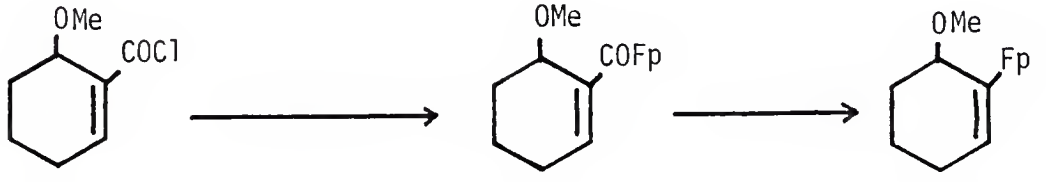
128 127

of (128) with NaH followed by MeI. Treatment of (127) with n-BuLi at -78°C followed by addition of CO_2 and acid work-up gave the acid (129)

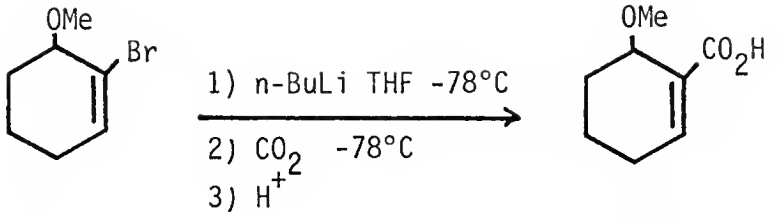
Scheme 6



128 127 129

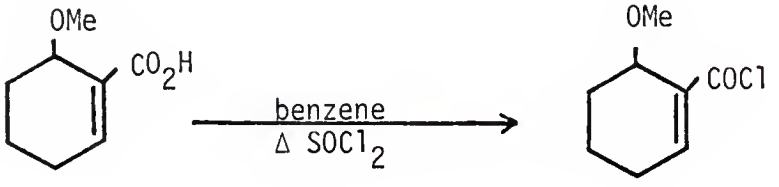


130 131 126



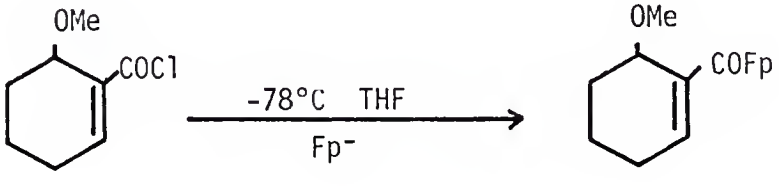
127 129

in a 33% yield. The acid (129) was then treated with $SOCl_2$ in benzene



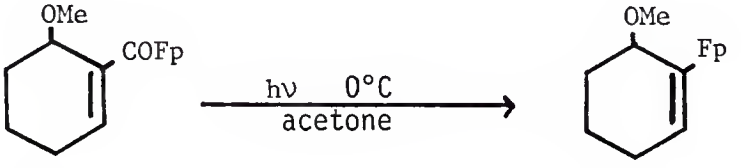
129 130

to give the acid chloride (130). Addition of the acid chloride (130)



130 131

to a suspension of Fp anion in THF at -78°C gave an 8% yield of the desired acyl complex (131) as an air-sensitive, brownish oil. The ^1H NMR spectrum of (131) is given in Figure 22. Photodecarbonylation of



131 126

(131) in d_6- acetone at 0°C gave an air-sensitive, brown oil (126) in a 70% yield. The ^1H NMR spectrum of (126) is given in Figure 23.

Now with (126) in hand the question of whether or not it would behave similarly to the reaction of (72) with $Me_3SiOSO_2CF_3$ remained to be answered.

Here it was found that treatment of (126) with $Me_3SiOSO_2CF_3$ at -78°C followed by warming to room temperature afforded a brownish oil (Figure 24) after removal of the solvent in vacuo. When NaI was added to a d_6-acetone solution of this oil an immediate color change, brown to purple, occurred. Work-up afforded FpI, 30% of cyclohexene (132) and 10% of 1,3-cyclohexadiene (133). A possible mechanism for formation of these products, which is similar to the C_7 manifold, is seen in Scheme 7.

In this mechanism addition of $Me_3SiOSO_2CF_3$ to (126) gives the allyl cation (134) which immediately hydride abstracts and rearranges to the π-complexes (96) and (137) via the same intermediate as seen in the C_7 manifold.

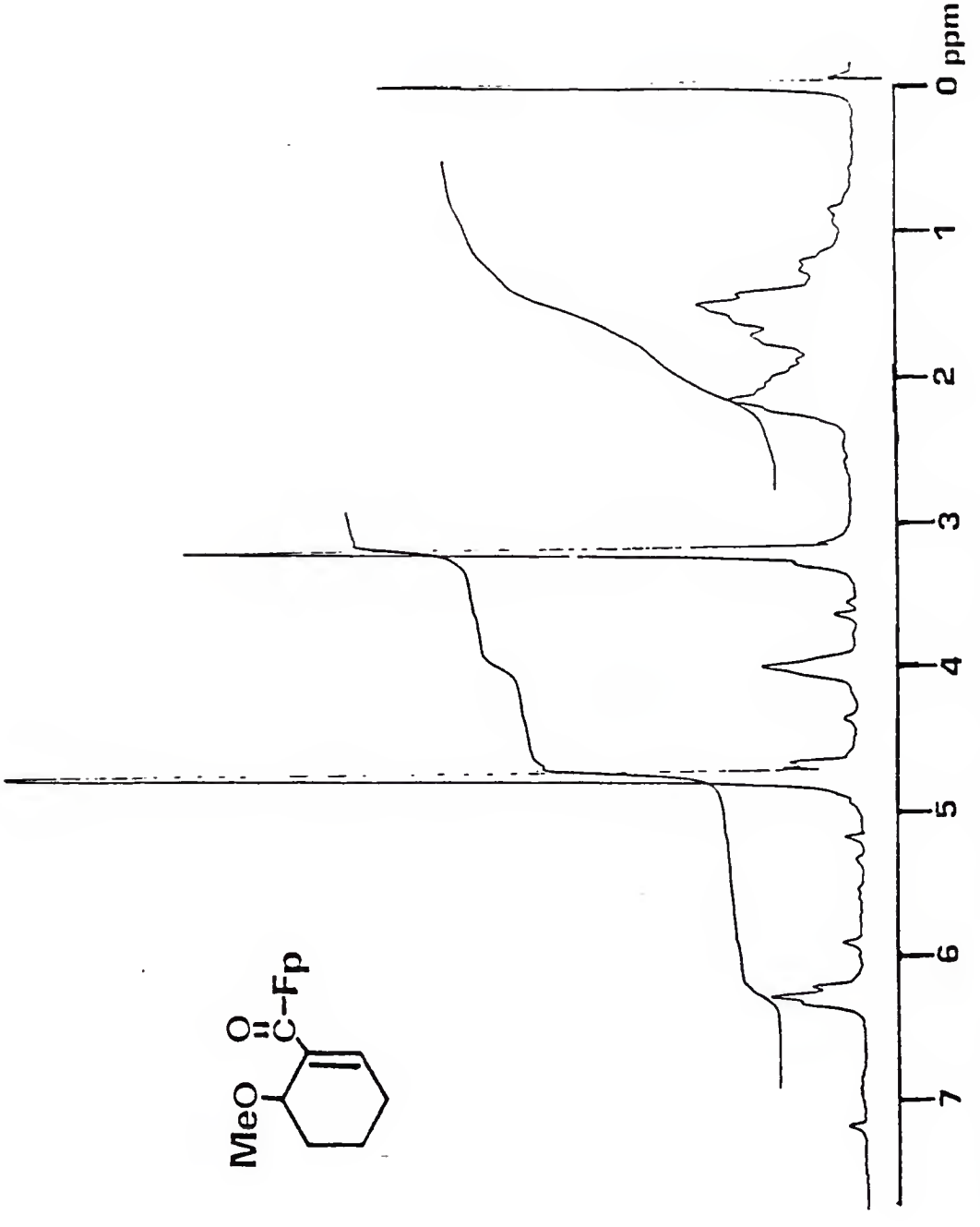


Figure 22. ^{1}H NMR spectrum of (131) in $CDCl_3$.

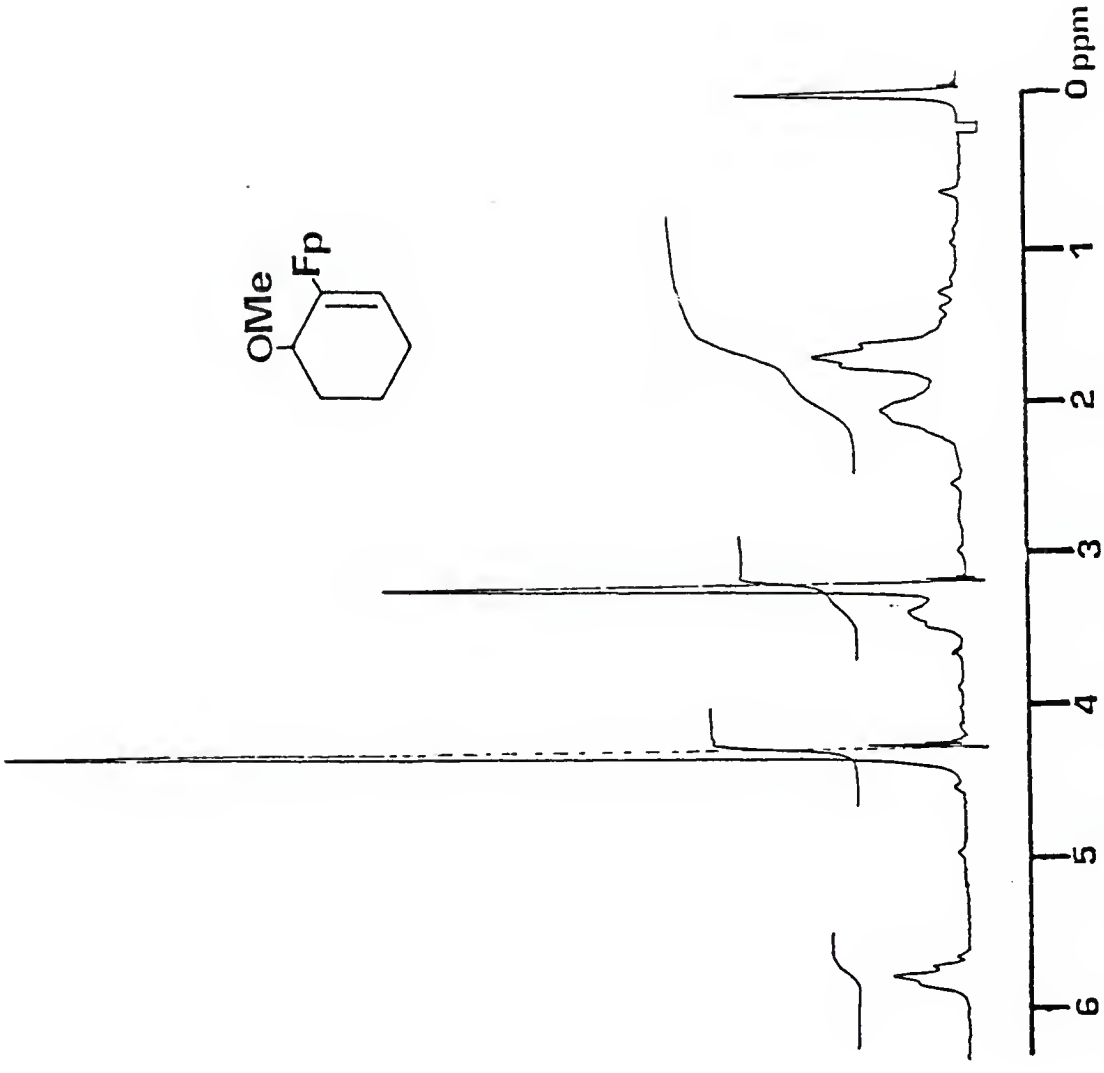


Figure 23. ^{1}H NMR spectrum of (126) in d_6-benzene.

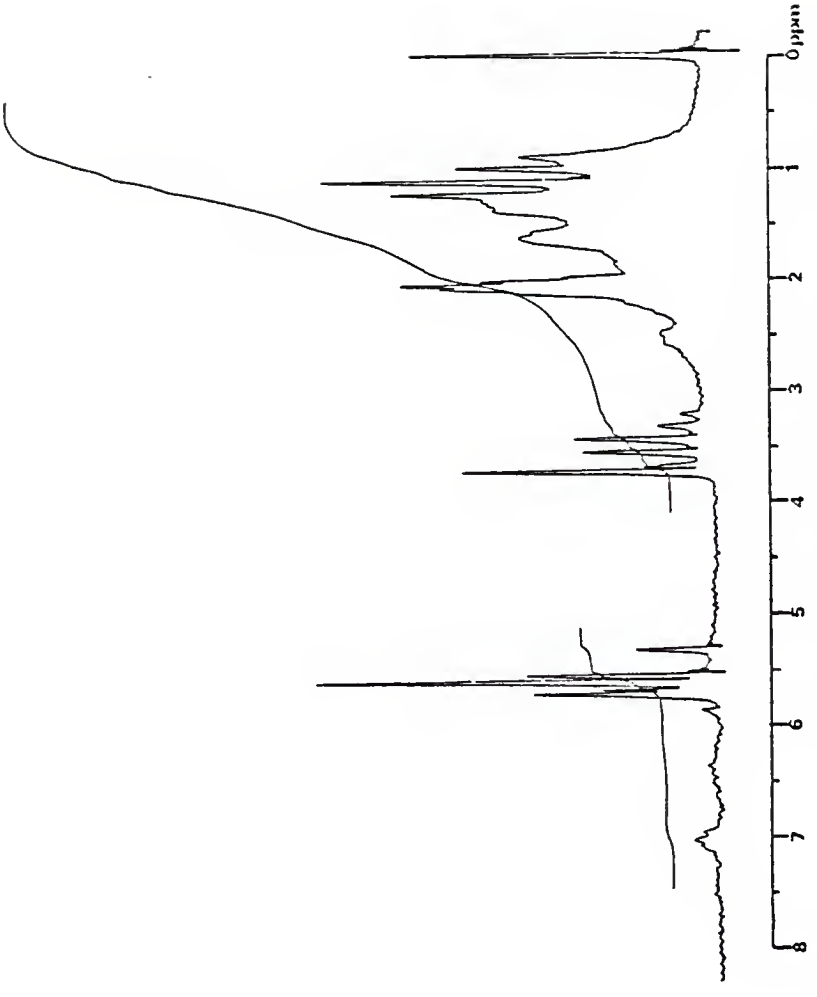
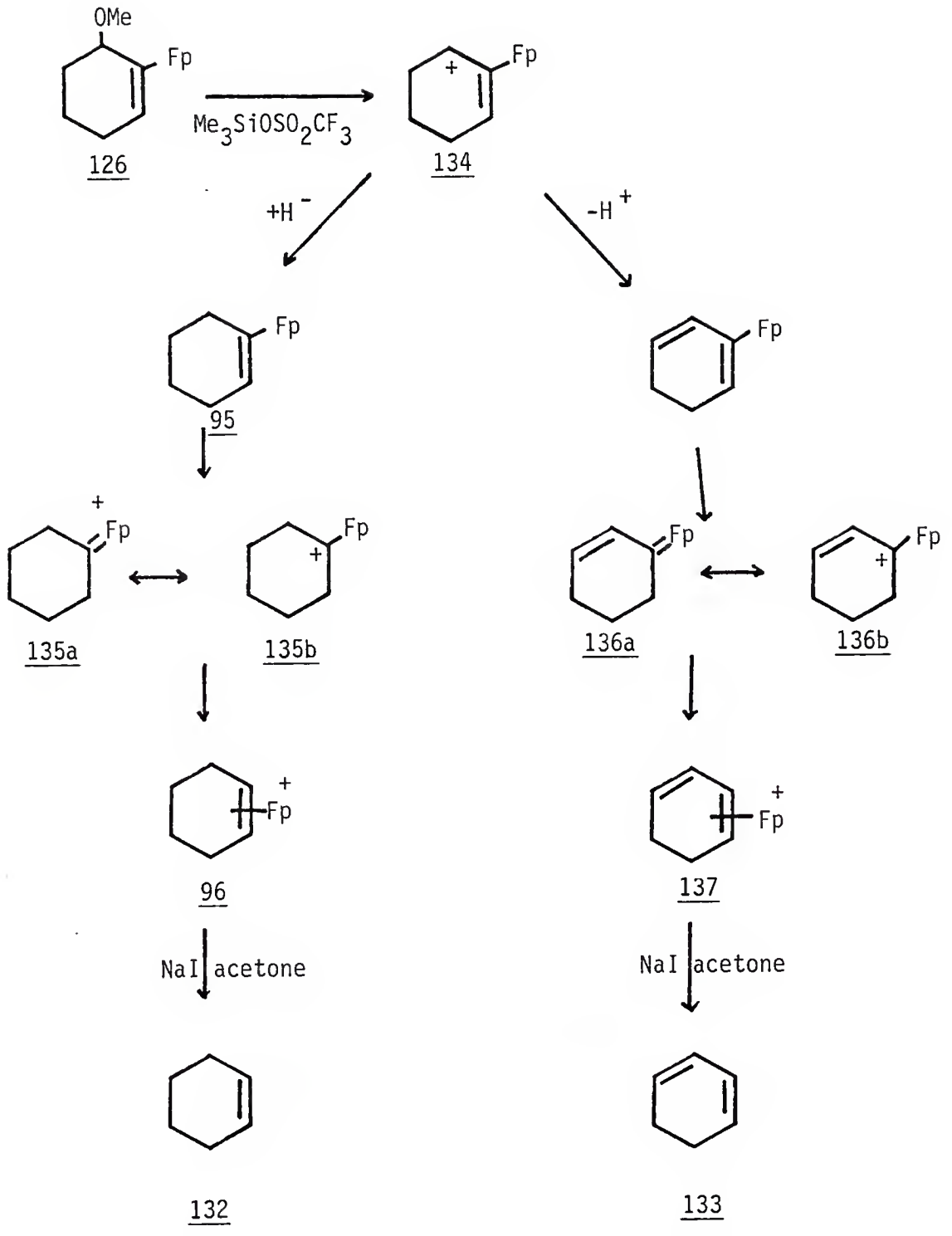


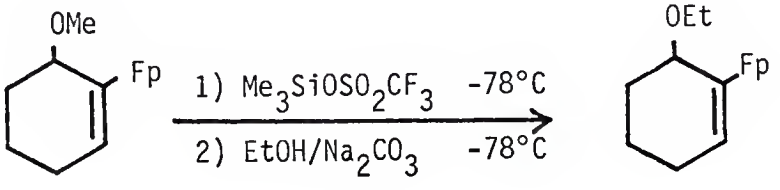
Figure 24. ^1H NMR spectrum of the crude products from the addition of $Me_3SiOSO_2CF_3$ to (126).

Scheme 7


OMe
Fp
126
$Me_3SiOSO_2CF_3$
Fp
134
$+H^-$
$-H^+$
Fp
95
Fp
Fp
135a
Fp
135b
Fp
136a
Fp
136b
Fp
96
Fp
137
NaI | acetone
NaI | acetone
132
133

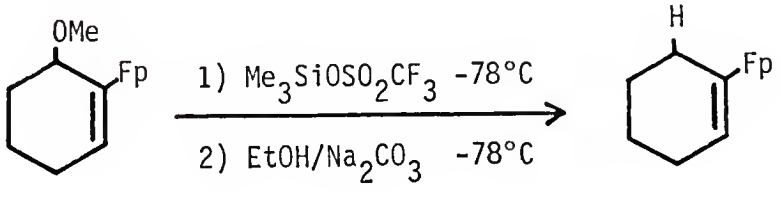
A further examination of the ^1H NMR spectrum (Figure 24) reveals resonances at δ 5.7 (Cp) and 5.45 (CH=CH) which is a good indication of structure (96) since the resonances overlap with the known π-complex (96) (Figure 25). The π-complex (137) was not isolated; however, as mentioned above addition of NaI to the reaction mixture (Figure 24) afforded FpI, cyclohexene, and 1,3-cyclohexadiene which is consistent with previous work.

Although the products obtained here were similar to the products obtained by the treatment of (72) with $Me_3SiOSO_2CF_3$, we decided to see if addition of $Me_3SiOSO_2CF_3$ to (126) followed by addition of $EtOH/Na_2CO_3$



126 138

would generate (138). In this case, and unlike (72), addition of $Me_3SiOSO_2CF_3$ to (126) did not give (138) but rather (95) in a 15% yield.



126 95

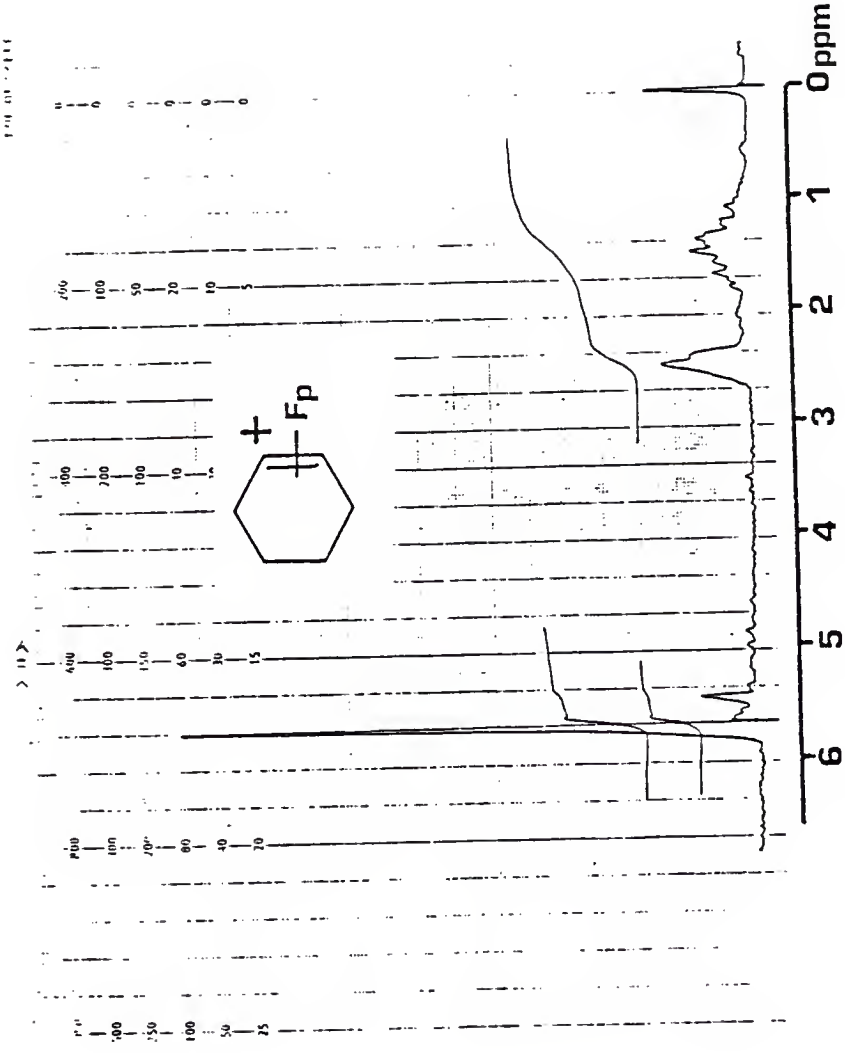
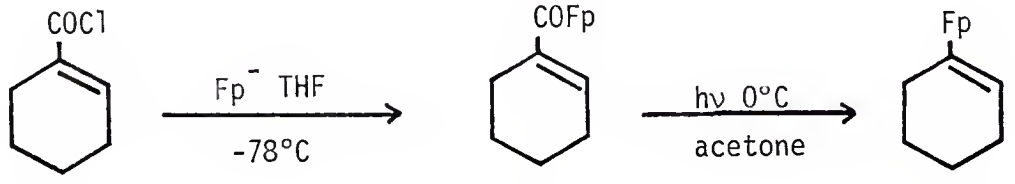


Figure 25. ^{1}H NMR spectrum of (96) in d_6-acetone.

This is, of course, the proposed cyclohexene precursor in Scheme 7. From this result it would appear that in the six member ring (126) very rapidly gives (95) which is protonated in a slow reaction. Thus, addition of base stopped the reaction at this point. To further prove the structure (95) an alternate synthesis was accomplished as seen below:



139 140 95

Addition of the acid chloride (139) to a suspension of Fp anion at -78°C gave the acyl complex (140) in a 69% yield. The acyl complex (140) was then photolyzed for 2.5 hours at 0°C in d_6-acetone to give a yellow, air-sensitive solid (95) in a 97% yield, which is consistent with the above work.

From these experiments it would appear that the allyl cation (134) is generated; however, if it rearranges to the allene complex (125) as seen in the C_7 manifold, the latter must very rapidly convert back to the cation to give the observed products.

In conclusion, the characterization and synthesis of the seven membered carbocyclic allene complex (35) has been described within this work. Further, it appears that this allene complex rather readily converts to the cation to give the carbocation products. As expected if

this conversion is accelerated by ring strain, the six membered ring gives the cation much faster. In fact, in this case the allene may not be formed at all. In addition, the chemistry of the substituted cyclopropyl acyl complexes was developed and found to be a useful route to sigma complexes by photolysis.

Further work is now being carried out on the conversion of the substituted cyclopropyl sigma complexes to the cyclopropylidene complex with hopes of observing its rearrangement to the allene complexes. Attempts are also under way to study the conversion of the sigma complex (72) to the allene complex (35) to see whether or not the allyl cation (33) is generated or whether (72) gives (35) via Fp assistance.

CHAPTER IV
EXPERIMENTAL

Chemicals

All solvents used were reagent grade. Methylene chloride was dried over P_4O_{10} and distilled under nitrogen. The tetrahydrofuran (THF) was dried over CaH_2-$LiAlH_4$ and distilled over Na-K alloy[61] immediately prior to usage. The benzene was refluxed over CaH_2 and distilled under nitrogen. The diethyl ether was dried over $LiAlH_4$ and distilled over Na-K alloy immediately prior to usage.

The alumina used for all column chromatography was Fisher certified neutral alumina, Brockman Activity I, to which 3% water was added.

All organometallic compounds were prepared under a nitrogen atmosphere either using Schlenk techniques[62] or by employing a glove box by Vacuum Atmosphere Inc. (recirculating under oxygen-free conditions).

Instrumentation

Proton magnetic resonance spectra were obtained with a Jeol FX-100 or Jeol PMX-60 spectrometer and referenced to tetramethylsilane (all chemical shifts are reported in units of δ). Infrared spectra were recorded on a Perkin Elmer 137 Spectrophotometer. Elemental analyses were performed by Atlantic Microlab; Atlanta, Georgia. All melting points were measured with a Thomas-Hoover melting point

apparatus and are uncorrected. Mass spectra were obtained on a AEI MS 30 spectrometer.

Photolyses were done with a 450 watt Hg Hanovia Lamp in a pyrex well. Transfer needles were ordered from Aldrich (stainless steel, double tip non-coring deflective 20 and 18 gauge).

The glpc analyses were carried out using a Varian Aerograph model 90-P gas chromatograph with thermal conductivity detector. Only one column was used in glpc work and is referred to as:

Column A - 20% SE-30 on Chromosorb, white, acid-washed, dimethyldichlorosilane; 80-100 mesh; 20 feet × 0.125 inches (copper tubing).

Quantitative analyses of the samples were obtained by the use of a calibration curve.[63] A measured amount of a standard (toluene) was added to weighed amounts of the desired compounds. In this manner 5 samples (an average of 3 injections per sample) containing different amounts of the desired compounds were prepared and analyzed by glpc. After the analysis, the area ratios were calculated (height × width at half-height) and a plot was made of the area ratios vs. weight ratios. The 5 data points were plotted and the best straight line was drawn by the use of a linear regression program on a Hewlett-Packard 85. This plot was then used to determine the weight ratio for a known area ratio. In turn, the weight of the unknown was determined.

Bis[(dicarbonyl-η^5-cyclopentadienyl)iron] [Fp_2] (45).

This compound was prepared in an 80% yield from iron pentacarbonyl and dicyclopentadiene according to the procedure of King and Stone.[64] ^{1}H NMR (d_6-acetone) δ 5.00 (s, Cp).

Potassium Dicarbonyl-η^5-cyclopentadienylferrate [Fp anion]

This compound was prepared from bis[(dicarbonyl-η^5-cyclopentadienyl)iron] and potassium tris(sec-butyl)borohydride in accordance with the procedure of Gladysz[65] (79% yield).

7-Chlorobicyclo[4.1.0]heptyl-7-carboxylic Acid Chloride (66).

To a solution of 7-chlorobicyclo[4.1.0]heptyl-7-carboxylic acid[66] (6.0 g; 0.03 moles) in benzene (10 mL) was added oxalyl chloride (7.0 g; 0.05 moles) dropwise with stirring. The reaction mixture was then stirred for 2 hours at room temperature at which time N,N-dimethylformamide (2 drops) was added. The mixture was then refluxed for 1.5 hours followed by the removal of the solvent (in vacuo) which left a dark oil. The oil was purified by vacuum distillation (0.3 torr; 80°-88°C) to give a colorless liquid (2.0 g; 28%): ^{1}H NMR ($CDCl_3$) δ 2.5-1.7 (m); IR (neat) 1780 cm^{-1} (CO).

7-Bromobicyclo[4.1.0]heptyl-7-carboxylic Acid Chloride (65).

To a solution of 7-bromobicyclo[4.1.0]heptyl-7-carboxylic acid[67] (3.0 g; 0.01 moles) in benzene (20 mL) was added N,N-dimethylformamide (2 drops) followed by an excess of oxalyl chloride. This was allowed to stir for 2 hours at room temperature followed by refluxing for 30 minutes. The solvent was removed in vacuo, to leave an orange oil (2.4 g; 87%): ^{1}H NMR ($CDCl_3$) δ 2.2-0.7 (m).

Trans-2,3-diphenylcyclopropanecarboxylic Acid Chloride (55).

To a mixture of trans-2,3-diphenylcyclopropanecarboxylic acid[68] (2.51 g; 0.01 moles) in chloroform (45 mL) with N,N-dimethylformamide (2 drops) was added oxalyl chloride (1.25 g; 0.01 moles) dropwise with stirring. This mixture was refluxed for 3 hours after which the solvent was removed to yield 2.31 g (86%) of a cream colored solid (mp. 185°-187°C).

Trans-2,3-diethylcyclopropanecarboxylic Acid Chloride (56).

To a mixture of trans-2,3-diethylcyclopropanecarboxylic acid[69a,b] (1.78 g; 0.01 moles) in chloroform (30 mL) with N,N-dimethylformamide (2 drops) was added oxalyl chloride (1.5 g; 0.01 moles) dropwise with stirring. This was refluxed for 3 hours followed by the removal of the solvent to yield 1.51 g (75%) of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 2.00-0.5 (m).

Dicarbonyl-η^5-cyclopentadienyl(cyclopropylcarbonyl)iron (51c).

A solution of cyclopropanecarboxylic acid chloride (2.00 g; 0.002 moles) in THF (5 mL) was added dropwise to a suspension of potassium η^5-cyclopentadienyldicarbonylferrate (3.00 g; 0.01 moles) in THF (30 mL) at 0°C under a N_2 atmosphere. The resulting mixture was then stirred for 1.5 hours at 0°C followed by 45 minutes at room temperature. The reaction mixture was then transferred (using a transfer needle) to a 100 mL round bottom flask containing 20 g of alumina (neutral; grade II) followed by the removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on an

alumina (neutral; grade II) column (1 inch × 6 inches) eluting with a mixture of hexane/CH_2Cl_2 (50/50).

The first band (red) was bis[(dicarbonylcyclopentadienyl)iron]. This was followed immediately by an orange band. Removal of the solvent in vacuo gave 0.682 g (20%) of an orange-brown, air-sensitive liquid. An analytical sample was prepared by further chromatographing the orange-brown liquid (½ inch × 2 inch column; elution with a mixture of hexane/CH_2Cl_2 (80/20); done in a dry box) to afford a brown, air-sensitive oil: ^1H NMR ($CDCl_3$) δ 5.0 (s, Cp, 5H), 2.75 (m, CH, 1H), 0.80 (m, CH_2, 4H); IR (neat) 3220, 3020, 2020, 1965, 1785, 1640, 1440, 1420, 1330, 1190, 1030, 940, 825, 680, 660, 620, 570 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 255.7 (bridging-CO), 214.0 (Fe-CO), 85.9 (Cp), 39.2 (C_1), 10.5 (C_2-C_3); MS m/e 218.0010 (calcd. M^+-CO, 218.0030); Anal. Found: C, 53.62; H, 4.19; Calcd. for $C_{11}H_{10}FeO_3$: C, 53.70; H, 4.09%.

Dicarbonyl-η^5-cyclopentadienyl(bicyclo[4.1.0]hepta-7-ylcarbonyl)iron (54).

To a cold (-78°C) stirred suspension of potassium η^5-cyclopentadienyldicarbonylferrate (2.587 g; 0.012 moles) in THF (30 mL) was added a solution of bicyclo[4.1.0]heptyl-7-carboxylic acid chloride[70] (1.90 g; 0.012 moles) in THF (20 mL) dropwise under a N_2 atmosphere. This was allowed to stir for 2 hours at -78°C followed by 5 hours at room temperature. The mixture was then transferred (using a transfer needle) to a 100 mL round bottom flask containing 25 g of alumina (neutral; grade II) followed by the removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on

an alumina (neutral; grade II) column (1 inch × 6 inches) eluting with a mixture of hexane/CH_2Cl_2 (80/20).

A red band was identified as bis[(dicarbonylcyclopentadienyl)iron]. This was followed immediately by a yellow band. Removal of the solvent in vacuo gave 0.650 g (18%) of a brown, air-sensitive solid (mp. 54°-56°C). An analytical sample was prepared by further chromatographing the brown solid [½ inch × 2½ inch column; elution with a mixture of hexane/CH_2Cl_2 (80/20); done in a dry box] to afford a brown, air-sensitive solid (mp. 56°-57°C; sealed tube): ^{1}H NMR ($CDCl_3$) δ 4.88 (s, Cp, 5H), 2.42 (m, H_7, 1H), 1.70 (m, 6H), 1.25 (m, 4H); IR (in $CDCl_3$) 2940, 2865, 2015, 1970, 1630, 1450, 1395, 1285, 1270, 1205, 1090, 1005, 905, 870, 730, 650, 570 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 253.0 (bridging-CO), 215.0 (Fe-CO), 85.9 (Cp), 54.3 (C_7), 24.7 (C_1 + C_6), 22.2 and 20.8 (C_2-C_5); MS m/e 272.0495 (Calcd. M^+-CO, 272.0499); Anal. Found: C, 59.79; H, 5.42. Calcd. for $C_{15}H_{16}FeO_3$: C, 60.03; H, 5.37%.

Reaction of Potassium η^5-Cyclopentadienyldicarbonylferrate with 7-Chlorobicyclo[4.1.0]heptyl-7-carboxylic Acid Chloride.

To a cold (0°C) suspension of potassium η^5-cyclopentadienyldicarbonylferrate (2.00 g; 9.6 mmoles) in THF (80 mL) was added dropwise a solution of 7-chlorobicyclo[4.1.0]heptyl-7-carboxylic acid chloride (3.50 g; 16.2 mmoles) in THF (20 mL) under a N_2 atmosphere. This mixture was allowed to stir 30 minutes at 0°C followed by 3 hours at room temperature. Work-up as above gave bis[(dicarbonylcyclopentadienyl)-iron] and 0.498 g (17%) of dicarbonyl-η^5-cyclopentadienyl(bicyclo-[4.1.0]heptyl-7-carbonyl)iron which gave NMR and IR spectra similar to those of (54).

Reaction of Potassium η^5-Cyclopentadienyldicarbonylferrate with 7-Bromobicyclo[4.1.0]heptyl-7-carboxylic Acid Chloride.

To a suspension of potassium η^5-cyclopentadienyldicarbonylferrate (2.00 g; 0.01 moles) in THF (60 mL) at 0°C was added dropwise a solution of 7-bromobicyclo[4.1.0]heptyl-7-carboxylic acid chloride (2.40 g; 0.008 moles) in THF (15 mL) under a N_2 atmosphere. This was allowed to stir 2 hours at 0°C followed by 1 hour at room temperature. Work-up as above gave bis[(dicarbonylcyclopentadienyl)iron] and 100 mg (3%) of dicarbonyl-η^5-cyclopentadienyl(bicyclo[4.1.0]heptyl-7-carbonyl)iron which gave IR and NMR spectra similar to those of (54).

Dicarbonyl-η^5-cyclopentadienyl(trans-2,3-diethylcyclopropylcarbonyl)-iron (53).[35]

To a suspension (at 0°C) of potassium η^5-cyclopentadienyldicarbonylferrate (2.012 g; 9.4 mmoles) in THF (20 mL) was added over 10 minutes a solution of trans-2,3-diethylcyclopropanecarboxylic acid chloride (1.012 g; 6.3 mmoles) in THF (10 mL) under a N_2 atmosphere. This mixture was allowed to stir for 2.5 hours at 0°C followed by 45 minutes at room temperature. The mixture was then transferred (using a transfer needle) to a 100 mL round bottom flask containing 20 g of alumina (neutral; grade II) followed by the removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (1 inch × 6 inches) eluting with a mixture of hexane/CH_2Cl_2 (80/20).

A red band was first collected which was bis[(dicarbonylcyclopentadienyl)iron]. This was followed immediately by a yellow band.

Removal of the solvent in vacuo gave 1.20 g (63%) of a brownish-orange, air-sensitive oil. An analytical sample was prepared by further chromatographing the brownish-orange oil [½ inch × 2 inch column; elution with a mixture of hexane/CH_2Cl_2 (80/20); done in a dry box] to afford an orange-brown, air-sensitive oil: ^1H NMR ($CDCl_3$) δ 4.80 (s, Cp, 5H), 2.50 (m, C_1, 1H), 1.20 (m, 12H); IR (neat) 2970, 2940, 2880, 2005, 1965, 1640, 1470, 1430, 1420, 1380, 1320, 1240, 1205, 1140, 1070, 1020, 985, 950, 830, 735, 660, 620, 580 cm^{-1}; decoupled ^{13}C NMR (d_6-acetone) δ 253.0 (bridging-CO), 214.4 (Fe-CO), 214.1 (Fe-CO), 86.0 (Cp), 53.7 (C_1), 35.8 (CH_3), 31.8 (CH_3), 26.5 (CH_2), 26.1 (CH_2), 14.1, 13.1 (C_2-C_3); MS m/e 274.0643 (Calcd. M^+-CO 274.0656); Anal. Found: C, 59.73; H, 6.05. Calcd. for $C_{15}H_{18}FeO_3$: C, 59.63; H, 6.01%.

Dicarbonyl-η^5-cyclopentadienyl(trans-2,3-diphenylcyclopropylcarbonyl)-iron (52).[35]

To a suspension of potassium η^5-cyclopentadienyldicarbonylferrate (2.10 g; 9.8 mmoles) in THF (35 mL) at 0°C was added a mixture of trans-2,3-diphenylcyclopropanecarboxylic acid chloride (1.56 g; 6.0 mmoles) in THF (20 mL) dropwise during 20 minutes under a N_2 atmosphere. This was allowed to stir 2.5 hours at 0°C followed by 45 minutes at room temperature. The mixture was then transferred (using a transfer needle) to a 100 mL round bottom flask containing 30 g of alumina (neutral; grade II) followed by the removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (1 inch × 5 inches) eluting with a mixture of hexane/CH_2Cl_2 (80/20).

A red band was first collected which was bis[(dicarbonylcyclopentadienyl)iron]. This was immediately followed by a yellowish band. Removal of the solvent gave 1.83 g (77%) of an orange-brown, air-sensitive oil. An analytical sample was prepared by further chromatographing the orange-brown oil [½ inch × 2 inch column; elution with a mixture of hexane/CH_2Cl_2 (80/20); done in a dry box] to afford an orange-brown, air-sensitive oil: ^1H NMR (d_6-acetone) δ 7.25 (s, aromatic, 10H), 4.85 (s, Cp, 5H), 3.50 (m, 2H), 3.12 (m, 1H); IR (d_6-acetone) 3110, 3090, 3060, 3040, 2255, 2010, 1955, 1705, 1635, 1500, 1450, 1420, 1310, 1250, 1155, 1080, 1020, 950, 920, 830, 790, 750, 735, 695, 580, 515 cm^{-1}; decoupled ^{13}C NMR (d_6-acetone) δ 249.8 (bridging-CO), 213.9 (Fe-CO), 213.8 (Fe-CO), 140.0, 135.6, 128.4, 129.1, 126.1, 125.8 (aromatic C's), 85.9 (Cp), 58.3 (C_1), 36.1 and 29.7 (C_2,C_3); MS m/e 314.0756 (Calcd. M^+-3CO, 314.0758); Anal. Found: C, 69.17; H, 4.64. Calcd. for $C_{23}H_{18}FeO_3$: C, 69.37; H, 4.56%.

Reaction of Potassium η^5-Cyclopentadienyldicarbonylferrate with Trans-2,3-diphenyl-1-chlorocyclopropanecarboxylic Acid Chloride

To a mixture of potassium η^5-cyclopentadienyldicarbonylferrate (0.500 g; 2.3 mmoles) at 0°C in THF (50 mL) was added a mixture of trans-2,3-diphenyl-1-chlorocyclopropanecarboxylic acid chloride (0.500 g; 1.7 mmoles) in THF (20 mL) dropwise during 30 minutes under a N_2 atmosphere. This was allowed to stir for 2.5 hours at 0°C followed by 45 minutes at room temperature. Work-up as above gave 0.104 g (15%) of dicarbonyl-η^5-cyclopentadienyl(trans-2,3-diphenylcyclopropylcarbonyl)-iron which gave NMR and IR spectra similar to those of (52).

Bicyclo[4.1.0]hepta-7-yldicarbonyl-η^5-cyclopentadienyliron (62).[27]

Dicarbonyl-η^5-cyclopentadienyl(bicyclo[4.1.0]hepta-7-ylcarbonyl)-iron (0.256 g; 0.86 mmoles) was dissolved in d_6-acetone (2 mL) under a N_2 atmosphere. This mixture was then filtered (under a N_2 atmosphere) into an NMR tube and then photolyzed at 0°C for 3 hours. The reaction mixture was then added to a 50 mL round bottom flask with 2 g of alumina (neutral; grade II) followed by removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (½ inch × 3 inches) eluting with hexane. Only one yellow band was collected which gave 0.122 g (52%) of an orange-brown, air-stable oil after the removal of the solvent. An analytical sample was prepared by further chromatographing the orange-brown oil [½ inch × 1 inch column; elution with hexane; done in a dry box] to afford an orange-brown, air-stable oil: ^{1}H NMR ($CDCl_3$) δ 4.70 (s, Cp, 5H), 1.70 (m), 1.2 (m), 0.56 (m); IR (neat) 2930, 2860, 2360, 2005, 1950, 1190, 1050, 900, 720 cm^{-1}; decoupled ^{13}C NMR (d_6-acetone) δ 205.8 (Fe-CO), 86.3 (Cp), 26.2, 22.1, 21.4 (C_1-C_6), 4.60 (C_7); MS m/e 272.0499, (Calcd. M^+, 272.0495); Anal. Found: C, 61.57; H, 5.97. Calcd. for $C_{14}H_{16}FeO_2$: C, 61.79; H, 5.93%.

Dicarbonyl-η^5-cyclopentadienyl(cyclopropyl)iron (28).[27]

Dicarbonyl-η^5-cyclopentadienyl(cyclopropylcarbonyl)iron (0.206 g; 0.84 mmoles) was dissolved in d_6-acetone (2 mL). This was filtered into an NMR tube (under a N_2 atmosphere) and photolyzed for 1 hour and 10 minutes at 0°C. The reaction mixture was then transferred (using a transfer needle) to a 50 mL round bottom flask containing 20 g of

alumina (neutral; grade II) followed by the removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (½ inch × 2 inches) eluting with hexane. Only one yellow band was collected to give 0.135 g (75%) of a brown-orange, air-stable oil. An analytical sample was prepared by further chromatographing the orange-brown oil [½ inch × 1 inch column; elution with hexane] to afford an orange-brown, air-stable oil: ^{1}H NMR (d_6-acetone) δ 4.90 (s, Cp, 5H), 0.58 (m, 3H), -0.05 (m, 2H) [these values correspond with the values reported by Cutler and co-workers[27]]; IR (neat) 3128, 3060, 2990, 2010, 1950, 1490, 1435, 1422, 1365, 1220, 1110, 1075, 1045, 1015, 1000, 925, 830, 635, 595, 585, 520, 465 cm^{-1}; decoupled ^{13}C NMR (d_6-acetone) δ 218.2 (Fe-CO), 86.9 (Cp), 8.60 (CH_2), -9.80 (CH); Anal. Found: C, 55.21; H, 4.68. Calcd. for $C_{10}H_{10}FeO_2$: C, 55.09; H, 4.62%.

Using d_6-benzene (2 mL) photolysis (2 hours) of 0.1127 g of the acyl complex gave 0.0518 g (52%) of isolated sigma complex.

Using petroleum ether (3 mL; 38°-56°C) photolysis (1 hour 45 minutes) of 0.1996 g of the acyl complex gave 0.265 g (16%) of isolated sigma complex.

Dicarbonyl-η^5-cyclopentadienyl(trans-2,3-diethylcyclopropyl)iron (61).[35]

Dicarbonyl-η^5-cyclopentadienyl(trans-2,3-diethylcyclopropyl-carbonyl)iron (0.5012 g; 1.65 mmoles) was dissolved in d_6-acetone (2 mL) and added to an NMR tube. The mixture was then photolyzed (under a N_2 atmosphere) for 2 hours at 0°C. The reaction mixture was then transferred (using a transfer needle) to a 100 mL round bottom flask with 4 g of alumina (neutral; grade II) followed by the removal of the

solvent in vacuo. The reaction products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (½ inch × 3 inches) eluting with hexane. Only one yellow band was collected which gave 0.3428 g (75%) of a brownish, air-sensitive oil. An analytical sample was prepared by further chromatographing the brownish, air-sensitive oil [½ inch × 2 inch column; elution with hexane; done in a dry box] to afford a brownish, air-sensitive oil: ^{1}H NMR ($CDCl_3$) δ 4.85 (s, Cp, 5H), 1.10 (m, 12H), 0.2 (m, 1H); IR (neat), 2960, 2940, 2880, 2860, 2000, 1950, 1455, 1375, 1300, 1250, 1200, 1170, 1020, 1000, 840, 825, 775, 635, 590, 560 cm^{-1}; decoupled ^{13}C NMR (d_6-acetone) δ 218.5 (Fe-CO), 218.2 (Fe-CO), 86.4 (Cp), 30.3, 30.1 (CH_2), 27.4 (CH_3), 15.1, 14.1 (C_2 + C_3), 7.5 (C_1); MS m/e 274.0657, (Calcd. M^+, 274.0656); Anal. Found: C, 61.49; H, 6.71. Calcd. for $C_{14}H_{18}FeO_2$: C, 61.34; H, 6.62%.

Dicarbonyl-η^5-cyclopentadienyl(trans-2,3-diphenylcyclopropyl)iron (60).[35]

Dicarbonyl-η^5-cyclopentadienyl(trans-2,3-diphenylcyclopropylcarbonyl)iron (0.50 g; 1.6 mmoles) was dissolved in d_6-acetone (2 mL) under a N_2 atmosphere. This mixture was then filtered into an NMR tube which was photolyzed (under a N_2 atmosphere) for 2 hours at 0°C. The reaction mixture was added to a 50 mL round bottom flask with 2 g of alumina (neutral; grade II) followed by the removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (½ inch × 3 inches) elution with hexane. Only one yellow band was collected which gave 0.45 g (97%) of an air-stable, orange solid (mp. 105°-107°C): ^{1}H NMR ($CDCl_3$) δ 7.12 (m, aromatic, 10H), 4.40 (s, Cp, 5H), 2.45 (cyclopropyl

H *trans* to Fp, d of d, $^{3}J_{\underline{cis}\ H's}$ = 5.2 Hz; $^{3}J_{\underline{trans}\ H's}$ = 2.3 Hz), 2.10 (cyclopropyl H *cis* to Fp, d of d), 1.50 (cyclopropyl H *alpha* to Fp, d of d); IR ($CDCl_3$) 3100, 3070, 3040, 3000, 2970, 2260, 2010, 1950, 1580, 1495, 1435, 1420, 1360, 1270, 1210, 1000, 910, 885, 830, 755, 730, 700, 635, 590, 570, 530 cm^{-1}; decoupled ^{13}C NMR (d_6-acetone) δ 216.4 (Fe-CO), 215.7 (Fe-CO), 145.8, 143.6, 129.2, 128.1, 127.7, 125.8, 125.2, 124.9 (aromatic C's), 85.1 (Cp), 34.9, 31.2 (C_2-C_3), 15.8 (C_1); MS m/e 314.0739 (Calcd. M^+ 314.0729); Anal. Found: C, 71.14; H, 4.94. Calcd. for $C_{22}H_{18}FeO_2$: C, 71.34; H, 4.90%.

Photolysis of 0.306 g of the acyl complex in d_6-benzene (2 mL) gave 0.148 g (64%) of the alkyl complex after 2.5 hours.

Using petroleum ether (2 mL; 38°-56°C) as the solvent, photolysis of 0.046 g of the acyl complex gave 0.022 g (51%) of the alkyl complex after 2.5 hours.

Attempted Synthesis of Dicarbonyl-η^5-cyclopentadienyl-7-chlorobicyclo-[4.1.0]heptyl-7-iron (64).

To a cold (-78°C) solution of 7,7-dichlorobicyclo[4.1.0]heptane[71] (3.10 g; 18.9 mmoles) in THF (15 mL) was added n-butyllithium (8.5 mL; 1.6 M solution in hexane) dropwise during 20 minutes under a N_2 atmosphere. This was allowed to stir 2 hours at -78°C followed by the addition of dicarbonylcyclopentadienyliron iodide (7.50 g; 24.7 mmoles) in THF (50 mL) dropwise over 10 minutes. This was allowed to stir 3 hours at -78°C followed by 12 hours at room temperature. The reaction was then transferred to a round-bottom flask (using a transfer needle) containing 30 g of alumina (neutral; grade II) followed by the removal of the solvent in vacuo. The reaction products coated on the

alumina were chromatographed on an alumina (neutral; grade II) column eluting with a mixture of hexane/CH_2Cl_2 (80/20).

The first yellow band gave a crude mixture of 7,7-dichlorobicyclo-[4.1.0]heptane and 7-chlorobicyclo[4.1.0]heptane. This was further purified by vacuum distillation (0.5 torr; 39°-43°C) to give 2.68 g of a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 2.00-1.00 (m); GC/MS m/e 130 (M^+ for 7-chlorobicyclo[4.1.0]heptane) and 164 (M^+ for 7,7-dichlorobicyclo-[4.1.0]heptane).[71,72]

The second yellow band gave 2.1 g of dicarbonyl-η^5-cyclopentadienyl(n-butyl)iron: ^{1}H NMR ($CDCl_3$) δ 4.70 (s, Cp, 5H), 1.40 (m), 0.90 (m); IR (neat) 2000 and 1950 cm^{-1} (CO's) (these values are consistent with known values).[73]

The third (red) band gave 1.6 g of bis[(dicarbonylcyclopentadienyl)iron]: ^{1}H NMR (d_6-acetone) δ 5.00 (s).

Reaction of 7,7-Dibromobicyclo[4.1.0]heptane with Potassium η^5-Cyclopentadienyldicarbonylferrate.

To a cold (-78°C) suspension of potassium η^5-cyclopentadienyldicarbonylferrate (3.02 g; 0.008 moles) in THF (30 mL) was added a solution of 7,7-dibromobicyclo[4.1.0]heptane[74] (1.10 g; 0.005 moles) in THF (15 mL) dropwise under a N_2 atmosphere. This was allowed to stir for 2 hours at -78°C followed by 31 hours at room temperature. The reaction was then transferred to a round bottom flask with 15 g of alumina (neutral; grade II) followed by the removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (1 inch × 4 inches) eluting with hexane.

The first yellow band gave a mixture of 7-bromobicyclo[4.1.0]-heptane[74] and 7,7-dibromobicyclo[4.1.0]heptane: GC/MS m/e 174 (M^+ for 7-bromobicyclo[4.1.0]heptane) and 252 (M^+ for 7,7-dibromobicyclo-[4.1.0]heptane); ^1H NMR ($CDCl_3$) δ 2.00-1.00 (m).

A second yellow band gave 0.35 g of bromocycloheptene:[75] ^1H NMR ($CDCl_3$) δ 6.20 (t, H_2, 1H), 2.75 (m), 2.25 (m), 1.80 (m).

The third band (red) gave 1.30 g of bis[(dicarbonylcyclopenta-dienyl)iron]: ^1H NMR (d_6-acetone) δ 5.00 (s).

Reaction of 7,7-Dichlorobicyclo[4.1.0]heptane with Potassium η^5-Cyclo-pentadienyldicarbonylferrate.

To a cold (-78°C) suspension of potassium η^5-cyclopentadienyldi-carbonylferrate (3.10 g; 0.014 moles) in THF (50 mL) was added a solu-tion of 7,7-dichlorobicyclo[4.1.0]heptane (2.86 q; 0.017 moles) in THF (10 mL) dropwise (under a N_2 atmosphere). This was allowed to stir for 1 hour at -78°C followed by 8 hours at room temperature. The reac-tion was then transferred to a round bottom flask (using a transfer needle) containing 24 g of alumina (nuetral; grade II) followed by the removal of the solvent in vacuo. The reaction products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (1 inch × 4 inches) eluting with hexane.

The first yellow band collected gave a mixture of 7,7-dichloro-bicyclo[4.1.0]heptane and 7-chlorobicyclo[4.1.0]heptane.[72] This was further purified by vacuum distillation (0.5 torr; 35°- 42°C) to give 1.25 g of a colorless liquid: ^1H NMR ($CDCl_3$) δ 2.00-1.00 (m); GC/MS m/e 130 (M^+ for 7-chlorobicyclo[4.1.0]heptane) and 164 (M^+ for 7,7-dichlorobicyclo[4.1.0]heptane).

The second band (red) gave 1.28 g of bis[(dicarbonylcyclopentadienyl)iron]: ^{1}H NMR (d_6-acetone) δ 5.00 (s).

Dicarbonyl-η^5-cyclopentadienyl(methoxymethyl)iron (71).[76]

A solution of dicarbonyl-η^5-cyclopentadienyl(2-methoxyacetyl)iron[37] (0.62 g; 0.03 moles) in d_6-acetone (2 mL) was filtered into an NMR tube (under a N_2 atmosphere). This was photolyzed for 3 hours at 0°C under a N_2 atmosphere. Work-up as described in the preparation of dicarbonyl-η^5-cyclopentadienyl(cyclopropyl)iron gave 0.48 g (87%) of a brown, air-sensitive oil: ^{1}H NMR (d_6-acetone) δ 4.85 (s, Cp, 5H), 4.76 (s, CH_2, 2H), 3.17 (s, OMe, 3H); IR (neat) 2010 and 1950 cm^{-1} (CO's); consistent with the known complex.[75]

Dicarbonyl-η^5-cyclopentadienyl(cyclohexenecarbonyl)iron (140).

To a cold (-40°C) suspension of potassium η^5-cyclopentadienyldicarbonylferrate (3.30 g; 0.015 moles) in THF (30 mL) was added a mixture of 1-cyclohexenecarbonyl chloride (2.00 g; 0.013 moles) in THF (10 mL) dropwise with stirring under a N_2 atmosphere. The reaction mixture was allowed to stir 1.5 hours at -40°C followed by 12 hours at room temperature at which time it was transferred to a 100 mL round bottom flask containing 10 g of alumina (neutral; grade II). The solvent was removed in vacuo and the products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (1 inch × 8 inches) eluting with a mixture of hexane/CH_2Cl_2 (80/20). The first band (red) was bis[(dicarbonylcyclopentadienyl)iron]. This was followed immediately by a yellow band. Removal of the solvent in vacuo gave

2.7428 g (69%) of a yellow, air-sensitive solid (mp. 73°-75°C). An analytical sample was prepared by further chromatographing the yellow, air-sensitive solid [½ inch × 1 inch column; elution with a mixture of hexane/CH_2Cl_2 (80/20); done in a dry box] to afford a yellow, air-sensitive solid (mp. 74°-75°C): ^{1}H NMR (d_6-acetone) δ 6.45 (m, H_2, 1H), 5.00 (s, Cp, 5H), 2.15 (m, CH_2's, 6H); IR ($CDCl_3$) 3160, 3130, 2940, 2860, 2840, 2250, 2005, 1960, 1780, 1450, 995, 960, 905, 830, 785, 725, 650, 610, 570, 500 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 2.52 (bridging-CO), 214.1 (Fe-CO), 152.3 (C_1), 137.3 (C_2), 85.5 (Cp), 25.2, 24.8, 21.9, 21.4 (C_3-C_6); MS m/e 258.0322 (Calcd. M^+-CO, 258.0343); Anal. Found: C, 58.71; H, 4.95. Calcd. for $C_{14}H_{14}FeO_3$: C, 58.77; H, 4.93%.

Dicarbonyl-η^5-cyclopentadienyl(cyclohexene)iron (95).

Dicarbonyl-η^5-cyclopentadienyl(cyclohexenecarbonyl)iron (0.4965 g; 1.7 mmoles) was dissolved in d_6-acetone (3 mL) under a N_2 atmosphere then filtered into an NMR tube. This mixture was then irradiated for 2.5 hours at 0°C. The product was then transferred (using a transfer needle) to a 50 mL round bottom flask containing ~3 g of alumina (neutral; grade II) followed by the removal of the solvent in vacuo. The products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (1 inch × 6 inches) eluting with hexane. Only one yellow band was collected and removal of the solvent gave 0.431 g (97%) of a yellow, air-sensitive solid (mp. 71°-72°C): ^{1}H NMR ($CDCl_3$) δ 5.60 (m, H_2, 1H), 4.78 (s, Cp, 5H), 2.20 (m, CH_2's, 4H), 1.55 (m, CH_2's, 4H); IR ($CDCl_3$) 3110, 3000, 2920, 2850, 2000, 1950, 1430, 1360, 1345, 1320, 1200, 1260, 1130, 1060, 1045, 1015, 1000, 910,

840, 830, 785, 735, 695, 630, 575, 465 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 216.8 (Fe-CO), 139.1 (C_1), 136.5 (C_2), 85.5 (Cp), 45.0 (C_6), 30.9 (C_3), 27.2, 23.5 (C_4 + C_5); MS m/e 258.0336 (Calcd. M^+, 258.0343); Anal. found: C, 60.35; H, 5.50. Calcd. for $C_{13}H_{14}FeO_2$: C, 60.50; H, 5.47%.

Dicarbonyl-η^5-cyclopentadienyl(cyclohexene)iron Hexafluorophosphate (96).

To a cold (-78°C) solution of dicarbonyl-η^5-cyclopentadienyl-(cyclohexene)iron (1.2035 g; 0.005 moles) in THF (20 mL) under a N_2 atmosphere was added a solution of tetrafluoroboric acid (0.902 g; a 62% solution in diethyl ether) dropwise over 15 minutes during which time a yellow precipitate formed. This was allowed to stir 2 minutes at -78°C followed by 30 minutes at room temperature. After filtration the precipitate was dried under high vacuum to give 1.573 g (97%) of a yellow solid: ^1H NMR (d_6-acetone) δ 5.70 (s + m, Cp and vinyl H's, 7H), 2.00 (m, CH_2's, 4H), 1.70 (m, CH_2's, 4H); IR (neat) 2040 and 1995 cm^{-1} (CO's); decoupled ^{13}C NMR (d_6-acetone) δ 209.7 (Fe-Co's), 126.2 (C_1 + C_2), 85.9 (Cp), 24.1, 21.8 (C_3-C_6); dec. 130 C (lit. 130 C) which is consistent with the known complex .[77]

Reaction of Dicarbonyl-η^5-cyclopentadienyl(cyclohexene)iron with Tetrafluoroboric Acid in the Presence of Trimethyl Phosphite.

To a cold (-78°C) solution of dicarbonyl-η^5-cyclopentadienyl-(cyclohexene)iron (0.6730 g; 0.002 moles) in ether (15 mL) under a N_2 atmosphere was added trimethyl phosphite (3.86 g; 0.03 moles) by

syringe. This was followed by the addition of tetrafluoroboric acid (5 mL; of a 62% solution in ether) dropwise over 5 minutes by syringe. This was allowed to stir for 1.5 hours at -78°C followed by 1.5 hours at room temperature. The crude mixture was transferred (using a transfer needle) to a 100 mL round bottom flask containing 10 g of alumina (neutral; grade II) and the solvent was removed in vacuo. The products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (½ inch × 4 inches) eluting with hexane. A single yellow band was collected. Removal of the solvent in vacuo gave 0.6351 g (72%) of a brown, air-sensitive oil: ^{1}H NMR (d_6-acetone) δ 5.15 (s, Cp, 5H), 3.70 (d, J_{P-H} = 11 Hz, 9H), 2.30 (m, CH_2's), 1.40 (m & d, J_{P-H} = 22 Hz); IR (neat) 2000 and 1945 cm^{-1} (CO's); decoupled ^{13}C NMR ($CDCl_3$) δ 217.6 (Fe-CO), 86.6 (Cp), 5.19 (P-OMe, J_{C-P} = 11 Hz), 42.2, 27.0, 26.8, 26.7 (C_2-C_6).

1-Bromo-7-methoxycycloheptene (75).

Method A

A mixture of 7,7-dibromobicyclo[4.1.0]heptane[71] (23 g; 0.07 moles) and silver nitrate (12.02 g; 0.11 moles) in dry methanol (300 mL) was refluxed for 5 hours under a N_2 atmosphere. The precipitate which formed was removed by filtration and 200 mL of CH_2Cl_2 and 300 mL of H_2O were added. The water layer was extracted with CH_2Cl_2 (2 × 100 mL) after which the combined organic layers were washed with H_2O (50 mL) and dried over $MsSO_4$. The filtrate was concentrated and purified by vacuum distillation (51°-53°C at 0.4 torr) to give 13.99 g (91%) of a colorless liquid. An analytical sample was prepared by a second distillation taking a cut at 52°C (0.4 torr): ^{1}H NMR ($CDCl_3$) δ 6.30

(t, H_2, 1H), 4.05 (m, H_7, 1H), 3.40 (s, OMe, 3H), 1.75 (m, CH_2's), 1.20 (m, CH_2's); IR (neat) 2920, 1700, 1650, 1450, 1365, 1310, 1200, 1160, 1120, 1095, 1050, 905, 890, 870, 850, 765, 730 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 135.6 (C_2), 125.7 (C_1), 84.9 (C_7), 56.6 (OMe), 29.6, 27.9, 25.9, 23.8 (C_3-C_6); MS m/e 171.9857 (M^+ Calcd. 171.9887); Anal. Found: C, 46.91; H, 6.40. Calcd. for $C_8H_{13}BrO$: C, 46.85; H, 6.39%.

Method B

To a cold (0°C) dispersion of sodium hydride (4.0 g of a 50% dispersion in oil washed 3 times with hexane) in THF (60 mL) was added a mixture of 2-bromocyclohepten-3-ol[38] (10 g) in THF (45 mL) dropwise with stirring under a N_2 atmosphere. This reaction mixture was allowed to stir 15 minutes at 0°C followed by 1 hour at room temperature after which the mixture was cooled to 0°C. To the reaction mixture was added CH_3I (15 mL) in THF (15 mL) dropwise during 10 minutes. After stirring 30 minutes at 0°C the reaction mixture was allowed to stir 9 hours at room temperature. Work-up as in Method A gave 4.455 g (41%) of 1-bromo-7-methoxycycloheptene.

Method C

Substitution of silver perchlorate for silver nitrate in a procedure that was otherwise the same as Method A gave 1-bromo-7-methoxycycloheptene in 97% yield.

7-Methoxycycloheptene-1-carboxylic Acid (78).

To a cold (-90°C) solution of 1-bromo-7-methoxycycloheptene (3.314 g; 0.016 moles) in THF (30 mL) under a N_2 atmosphere was added

n-butyllithium (11.5 mL of a 1.6 M solution in hexane) dropwise during 10 minutes with stirring. The temperature was not allowed to exceed -80°C. The mixture was stirred for 1.5 hours at -80°C after which the mixture was added slowly to dry ice (by means of a transfer needle) in a 500 mL Erlenmeyer flask under a stream of N_2. This was then allowed to stir for 1 hour at room temperature after which it was added to a mixture of CH_2Cl_2 (200 mL) and was then acidified with dilute H_2SO_4. The water layer was extracted 2 times with CH_2Cl_2 (200 mL) (do not use diethyl ether) followed by drying the organic layer over $MgSO_4$. Removal of the solvent in vacuo afforded 1.80 g (66%) of a white solid (mp. 59°-62°C) which was used without further purification: ^1H NMR ($CDCl_3$) δ 11.6 (s, 1H), 7.50 (t, H_2, 1H), 4.55 (d, H_7, 1H), 3.30 (s, OMe, 3H), 2.70-0.60 (m, CH_2, 8H); IR (neat) 2930, 2640, 1680, 1640, 1430, 1270, 1190, 1090, 1055, 1010, 900, 725, 705 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 172.5 (CO), 150.4 (C_2), 134.5 (C_1), 74.5 (C_7), 55.8 (OMe), 29.3, 27.5, 25.8, 23.9 (C_3-C_6); Anal. Found: C, 63.31; H, 8.40. Calcd. for $C_9H_{13}O_3$: C, 63.49; H, 8.29%.

7-Methoxycycloheptene-1-carboxylic Acid Chloride (79).

To a stirred solution of 7-methoxycycloheptene-1-carboxylic acid (3.2550 g; 0.02 moles) in benzene (30 mL) at room temperature was added thionyl chloride (3.520 g; 0.02 moles) dropwise during 3 minutes under a N_2 atmosphere. The reaction mixture was allowed to stir for 2 hours at room temperature at which time 2 drops of N,N-dimethylformamide was added followed by refluxing for 2 hours after which the solvent was removed in vacuo to afford a brownish oil. This was purified by vacuum distillation (75°-80°C; 0.03 torr) to give 2.504 g (70%) of a colorless

liquid: ^{1}H NMR ($CDCl_3$) δ 7.75 (t, H_2, 1H), 4.50 (d, H_7, 1H), 3.30 (s, OMe, 3H), 2.30-0.50 (m, CH_2, 8H); IR (neat) 3000, 1750, 1450, 1380, 1340, 1220, 1170, 1120, 1090, 1030, 960, 905, 865, 820, 780 cm^{-1}.

Dicarbonyl-η^5-cyclopentadienyl(7-methoxycycloheptene-1-carbonyl)iron (74).

To a stirred suspension of potassium η^5-cyclopentadienyldicarbonylferrate (2.90 g; 0.01 moles) in THF (50 mL) at -78°C was added a mixture of 7-methoxycycloheptene-1-carboxylic acid chloride (2.3120 g; 0.01 moles) in THF (30 mL) dropwise during 10 minutes under a N_2 atmosphere. This mixture was allowed to stir for 1 hour at -78°C followed by 17 hours at room temperature at which time it was transferred to a 100 mL round bottom flask containing 10 g of alumina (neutral; grade II). The solvent was removed in vacuo and the products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (1 inch × 8 inches) eluting with a mixture of hexane/CH_2Cl_2 (80/20). The first band (red) was bis[(dicarbonylcyclopentadienyl)iron]. This was followed immediately by a yellow band. Removal of the solvent in vacuo gave 1.102 g (27%) of a brownish, air-sensitive oil. An analytical sample was prepared by further chromatographing the brownish oil [½ inch × 2 inch column; elution with a mixture of hexane/CH_2Cl_2 (80/20); done in a dry box] to afford a brown, air-sensitive oil: ^{1}H NMR ($CDCl_3$) δ 6.45 (m, H_2, 1H), 4.90 (s, Cp, 5H), 4.20 (m, H_7, 1H), 3.20 (s, OMe, 3H), 2.90-1.00 (m, CH_2's, 8H); IR (neat) 3110, 2930, 2860, 2820, 2010, 1960, 1600, 1450, 1440, 1370, 1340, 1315, 1220, 1200, 1165, 1120, 1090, 1025, 1000, 970, 885, 830, 710, 680, 630, 570, 510 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 252.7 (bridging-CO), 214.2 (Fe-CO), 158.1 (C_1), 144.4 (C_2),

85.8 (Cp), 75.7 (C_7), 55.8 (OMe), 29.7, 26.7, 26.1, 24.2 (C_3-C_6); MS m/e 302.0588 (M^+-CO, Calcd. 302.0604); Anal. Found: C, 58.05; H, 5.68. Calcd. for $C_{16}H_{18}FeO_4$: C, 58.21; H, 5.50%.

It was also found at the time of chromatographing the crude mixture one could elute with hexane only (150 mL; one yellow band came down which was not collected) followed by eluting with pure CH_2Cl_2. This gave 2 bands (a reddish and a yellowish band) which were collected together in a 500 mL round bottom flask. Removal of the solvent in vacuo gave a mixture of Fp_2 and the desired acyl complex which was used without further purification.

Dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron (72).

A solution of dicarbonyl-η^5-cyclopentadienyl(7-methoxycyclo-heptene-1-carbonyl)iron (1.102 g; 3.4 mmoles) in d_6-acetone (2 mL) was photolyzed under nitrogen for 3 hours at 0°C. The product was then coated on alumina (neutral; grade II) and chromatographed on an alumina (neutral; grade II) column (½ inch × 2 inches) eluting with hexane. Only one yellow band was collected and removal of the solvent gave 0.536 g (53%) of a brownish, air-sensitive oil. An analytical sample was prepared by further chromatographing the brown, air-sensitive oil (½ inch × 1 inch column; eluting with hexane; done in a dry box) to afford a brown, air-sensitive oil: ^1H NMR ($CDCl_3$) δ 5.80 (t, H_2, 1H), 4.75 (s, Cp, 5H), 3.80 (m, H_7, 1H), 3.30 (s, OMe, 3H), 2.50-0.80 (m, CH_2's, 8H); IR (neat) 3110, 2930, 2980, 2850, 2820, 2010, 1920, 1785, 1585, 1440, 1365, 1330, 1265, 1235, 1205, 1145, 1100, 1070, 1050, 1020, 1000, 825, 800, 780, 720, 630, 575 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 216.7 (Fe-CO's), 147.8 (C_1), 140.7 (C_2), 90.3 (C_7), 85.4

(Cp), 56.1 (OMe), 31.7, 29.6, 27.5, 27.2 (C_3-C_6); MS m/e 302.0670 (Calcd. M^+, 302.0605); Anal. Found: C, 59.38; H, 6.10. Calcd. for $C_{15}H_{18}FeO_3$: C, 59.63; H, 6.00%.

The crude mixture of Fp_2 and acyl complex (from above) was dissolved in acetone (~10 mL) in a N_2 atomosphere. This mixture was added to a pyrex tube (9 inches × 1 inch [diam]) and photolyzed for 7 hours at 0°C (occasional shaking) followed by a work-up (column; ½ inch × 4 inches) identical to that above.

Attempted Synthesis of Dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron.

To a dry Schlenk tube (equipped with a magnetic stirrer) was added 1-bromo-7-methoxycycloheptene (1.502 g; 0.005 moles) in THF (30 mL). This was cooled to -78°C at which time n-butyllithium (5.2 mL of a 1.6 M solution in hexane) was added dropwise under a N_2 atmosphere. This was allowed to stir for 45 minutes (at -78°C) at which time a mixture of dicarbonyl-η^5-cyclopentadienyliron iodide (2.5 g; 0.008 moles) in THF (30 mL) was added by syringe dropwise. This mixture was allowed to stir for 45 minutes at -78°C followed by 6 hours at room temperature. The products were coated on alumina (neutral; grade II) and chromatographed on an alumina (neutral; grade II) column (1 inch × 5 inches) under a N_2 atmosphere with hexane. The first band (yellow) gave 1.02 g of 7-methoxy-1-iodocycloheptene: ^1H NMR ($CDCl_3$) δ 6.8 (t, H_2, 1H), 4.05 (m, H_7, 1H), 3.40 (s, OMe, 3H), 2.5-0.80 (m); ^{13}C NMR decoupled ($CDCl_3$) δ 143.9 (C_2), 103.7 (C_1), 86.6 (C_7), 56.8 (OMe), 30.3, 29.7, 25.7, 24.7 (C_3-C_6); MS m/e 252.0074 (Calcd. M^+ 252.0011).

The second band (red) gave dicarbonyl-η^5-cyclopentadienyliron iodide: ^1H NMR (d_6-acetone) δ 5.20 (s).

1-Bromo-7-ethoxycycloheptene (109).

A mixture of 7,7-dibromobicyclo[4.1.0]heptane (40.0 g; 0.12 moles), silver nitrate (25.0 g; 0.14 moles) and absolute ethyl alcohol (250 mL) in a 1 L round-bottom flask was refluxed for 15 hours under a N_2 atmosphere. The formed precipitate was removed by filtration and the filtrate was added to a mixture of CH_2Cl_2/H_2O (200 mL/300 mL). The water layer was extracted 2 times with CH_2Cl_2 (100 mL) at which time the organic layers were washed with water (100 mL) and dried over $MgSO_4$. The solution was filtered and the solvent was removed in vacuo. The product was further purified by vacuum distillation (54°-55°C; 0.4 torr) to give 19.62 g (75%) of a yellowish liquid. An analytical sample was further prepared by a second distillation taking a cut at 55°C (0.4 torr): ^{1}H NMR ($CDCl_3$) δ 6.45 (t, H_2, 1H), 4.20 (d, H_7, 1H), 3.80 (d of t, OCH_2-, 2H), 1.80 (m, CH_2's), 1.25 (t, CH_3); IR (neat) 2980, 2930, 2860, 1740, 1640, 1550, 1440, 1395, 1370, 1305, 1270, 1160, 1090, 900, 860, 820, 775, 730 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 135.6 (C_2), 126.7 (C_1), 83.2 (C_7), 64.4 (OCH_2-), 30.1, 28.1, 26.0, 24.1 (C_3-C_6), 15.3 (CH_3); MS m/e 218.03065 (Calcd. M^+ 218.03063); Anal. Found: C, 49.44; H, 6.93. Calcd. for $C_9H_{15}BrO$: C, 49.33; H, 6.90%.

7-Ethoxycycloheptene-1-carboxylic Acid (110).

The method used to prepare 7-methoxycycloheptene-1-carboxylic acid was also used for this compound, starting with 1-bromo-7-ethoxycycloheptene (12 g; 0.05 moles) in THF (100 mL) and n-butyllithium (40 mL; 1.6 M in hexane). A yield of 6.532 g (65%) of a yellowish oil was obtained and was used without further purification: ^{1}H NMR ($CDCl_3$) δ

11.80 (s, 1H), 7.40 (t, H_2, 1H), 4.60 (d, H_7, 1H), 3.50 (q, OCH_2-, 2H), 3.00-0.70 (m, CH_2's & CH_3); IR (neat) 2920, 2610, 2520, 1680, 1420, 1260, 1210, 1090, 975, 925, 870, 750, 710 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 172.9 (CO), 150.5 (C_2), 134.9 (C_1), 72.6 (C_7), 63.5 (OCH_2-), 29.7, 27.6, 25.8, 24.0 (C_3-C_6), 15.1 (CH_3).

7-Ethoxycycloheptene-1-carboxylic Acid Chloride (111).

This compound was prepared by a route identical to that used for 7-methoxycycloheptene-1-carboxylic acid chloride, starting with 7-ethoxycycloheptene-1-carboxylic acid (6.02 g; 30 mmoles) and an excess of thionyl chloride. This gave 3.65 g (55%) of a brownish oil which was used without further purification: ^1H NMR ($CDCl_3$) δ 7.65 (t, H_2, 1H), 4.50 (d, H_7, 1H), 3.45 (q, OCH_2-, 2H), 1.70 (m, CH_2's & CH_3); IR (neat) 2940, 2860, 1750, 1640, 1440, 1380, 1340, 1270, 1220, 1180, 1120, 1095, 1000, 960, 930, 895, 810, 750, 720 , 685 cm^{-1}.

Dicarbonyl-η^5-cyclopentadienyl(7-ethoxycycloheptene-1-carbonyl)iron (112).

To a stirred suspension of potassium η^5-cyclopentadienyldicarbonylferrate (4.6 g; 0.02 moles) in THF (100 mL) at -78°C was added a solution of 7-ethoxycycloheptene-1-carboxylic acid chloride (3.0 g; 0.02 moles) in THF (10 mL) dropwise over 10 minutes under a N_2 atmosphere. This mixture was allowed to stir 25 minutes at -78°C and 13 hours at room temperature, followed by usual work-up as in the preparation of dicarbonyl-η^5-cyclopentadienyl(7-methoxycycloheptene-1-carbonyl)iron.

The first band (red) was bis[(dicarbonylcyclopentadienyl)iron]. This was immediately followed by a yellow band. Removal of the solvent in vacuo gave a brownish, air-sensitive oil which was used without further purification: ^{1}H NMR (d_6-acetone) δ 6.60 (t, H_2, 1H), 5.00 (s, Cp, 5H), 4.20 (m, H_7, 1H), 3.30 (q, OCH_2-, 2H), 1.50 (m, CH_2's & CH_3); IR (neat) 3050, 2920, 2860, 2000, 1970, 1600, 1440, 1350, 1080, 830, 740, 720, 670, 630, 570 cm^{-1}.

Dicarbonyl-η^5-cyclopentadienyl-η^1-(7-ethoxy-1-cycloheptenyl)iron (108).

A solution of the dicarbonyl-η^5-cyclopentadienyl(7-ethoxycyclo-heptene-1-carbonyl)iron in acetone (10 mL) was photolyzed for 2 hours at 0°C (under a N_2 atmosphere). The usual work-up as in the preparation of dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)-iron gave 1.205 g (28% from the acid chloride) of a brownish, air-sensitive oil. An analytical sample was further prepared by chromatographing the brown oil (½ inch × 2 inch column; elution with hexane; done in a dry box) to afford a brown, air-sensitive oil: ^{1}H NMR ($CDCl_3$; Figure 11) δ 8.50 (t, H_2, 1H), 4.90 (s, Cp, 5H), 4.00 (m, H_7, 1H), 3.45 (q, OCH_2-, 2H), 1.55 (m, CH_2's & CH_3); IR (neat) 3100, 2990, 2920, 2850, 2005, 1950, 1580, 1440, 1370, 1345, 1260, 1190, 1180, 1080, 1000, 820, 630, 570 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 216.8 (Fe-CO), 148.9 (C_1), 140 (C_2), 87.9 (C_7), 85.3 (Cp), 63.4 (OCH_2-), 31.7, 30.3, 27.6, 27.4 (C_3-C_6), 15.7 (CH_3); MS m/e 316.0771 (Calcd. M^+ 316.0761); 288.0815 (Calcd. M^+-CO 288.0812); Anal. Found: C, 60.95; H, 6.43. Calcd. for $C_{16}H_{20}FeO_3$: C, 60.78; H, 6.38%.

1-Bromo-6-methoxycyclohexene (127).

To a dispersion of sodium hydride (2.00 g of a 50% dispersion in oil was washed 3 times with hexane) in THF (100 mL) at 0°C was added a mixture of 2-bromocyclohexen-3-ol[38] [6.60 g; 0.04 moles) in THF (10 mL) dropwise during 10 minutes] with stirring under a N_2 atmosphere. The reaction mixture was allowed to stir 30 minutes at 0°C followed by 1 hour at room temperature. This mixture was then cooled to 0°C at which time CH_3I (6 mL; 0.1 moles) was added dropwise while stirring. After stirring 30 minutes at 0°C the mixture was allowed to stir 9 hours at room temperature at which time the crude mixture was added to CH_2Cl_2 (200 mL) overlaid with H_2O (200 mL). The water layer was extracted 2 times with 50 mL of CH_2Cl_2 at which time the combined organic layers were washed with H_2O (50 mL) and dried over $MgSO_4$. The filtrate was concentrated and purified by vacuum distillation (42°-45°C; 0.3 torr) to give 11.02 g (64%) of a colorless liquid. An analytical sample was prepared by a second distillation taking a cut at 42°C (0.2 torr): ^1H NMR ($CDCl_3$) δ 6.20 (m, H_2, 1H), 3.75 (m, H_6, 1H), 3.40 (s, OMe, 3H), 1.80 (m, CH_2's, 5H), 1.10 (m, CH_2's); IR (neat) 2940, 2820, 1690, 1640, 1450, 1360, 1330, 1190, 1090, 985, 940, 905, 855, 830, 800, 740 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 204.5 (C_2), 194.0 (C_1), 149.8 (C_6), 128.5 (OMe), 99.7, 99.0, 88.3 (C_3-C_5); MS m/e 189.9983 (M^+ Calcd. 189.9993); Anal. Found: C, 44.02; H, 5.83. Calcd. for $C_7H_{11}BrO$: C, 44.00; H, 5.80%.

6-Methoxycyclohexene-1-carboxylic Acid (129).

To a cold (-78°C) solution of 1-bromo-6-methoxycyclohexene (6.012 g; 0.03 moles) in THF (40 mL) was added n-butyllithium (23 mL; 1.6 M

in hexane) dropwise while stirring during 10 minutes. The reaction mixture was allowed to stir for 1 hour at -78°C at which time the solution was added to an excess amount of CO_2 slowly over 10 minutes using a transfer needle. The mixture was allowed to stir for 2 hours at room temperature followed by the addition of a mixture of H_2O/ CH_2Cl_2 (200/200 mL). The water layer was extracted 2 times with 100 mL of CH_2Cl_2 followed by the acidification of the H_2O layer with dilute H_2SO_4. The water layer was then extracted 2 times with 50 mL of CH_2Cl_2 (do not use ether) followed by drying the organic layer over $MgSO_4$. Removal of the solvent in vacuo afforded 1.60 g (33%) of a cream colored solid (mp. 106°-107°C, recrystallized from ethanol). An analytical sample was prepared by further recrystallization from ethanol followed by vacuum drying for 3 hours (mp. 107°-108°C): ^1H NMR (d_6-acetone) δ 10.30 (s, 1H), 7.40 (t, H_2, 1H), 4.50 (d, H_6, 1H), 3.20 (s, OMe, 3H), 2.70 (m, CH_2's, 6H); IR (neat) 2940, 1685, 1640, 1420, 1275, 1190, 1160, 1070, 900, 760, 640 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 171.5 (CO), 145.8 (C_2), 130.0 (C_1), 70.3 (C_6), 56.8 (OMe), 25.9, 25.7, 15.7 (C_3-C_5); Anal. Found: C, 61.41; H, 7.78. Calcd. for $C_8H_{12}O_3$: C, 61.52; H. 7.75%.

6-Methoxycyclohexene-1-carboxylic Acid Chloride (130).

A stirred solution of 6-methoxycyclohexene-1-carboxylic acid (1.60 g; 0.01 moles) in benzene (30 mL) at room temperature was added to excess thionyl chloride (~2.5 g) dropwise during 5 minutes under a N_2 atmosphere. The reaction mixture was allowed to stir 10 hours at room temperature at which time the thionyl chloride and benzene were removed in vacuo to give a brownish colored oil (used without further

purification): ^{1}H NMR ($CDCl_3$) δ 6.30 (m, H_2, 1H), 3.80 (m, H_6, 1H), 3.40 (s, OMe, 3H), 1.70 (m); IR (Neat) 2940, 2720, 1750, 1640, 1440, 1420, 1360, 1350, 1250, 1190, 1090, 1070, 980, 920, 870, 820, 710 cm^{-1}.

Dicarbonyl-η^5-cyclopentadienyl(6-methoxycyclohexene-1-carbonyl)iron (131).

To a stirred suspension of potassium η^5-cyclopentadienyldicarbonylferrate (2.96 g; 0.01 moles) in THF (60 mL) at -78°C was added a mixture of 6-methoxycyclohexene-1-carboxylic acid chloride (2.0 g; 0.01 moles) in THF (20 mL) dropwise during 10 minutes under a N_2 atmosphere. This was allowed to stir 45 minutes at -78°C followed by 4 hours at room temperature, at which time it was transferred to a 100 mL round bottom flask containing 20 g of alumina (neutral; grade II). The solvent was removed in vacuo and the products coated on the alumina were chromatographed on an alumina (neutral; grade II) column (1 inch × 6 inches) eluting with a mixture of hexane/CH_2Cl_2 (80/20). The first band (red) was bis[(dicarbonylcyclopentadienyl)iron]. This was immediately followed by a yellow band. Removal of the solvent in vacuo gave 0.256 g (8%) of a yellow-orange oil which was used without further purification: ^{1}H NMR ($CDCl_3$; Figure 22) δ 6.40 (m, H_2, 1H), 4.80 (s, Cp, 5H), 4.10 (m, H_6, 1H), 3.30 (s, OMe, 3H), 2.2 (m), 1.5 (m); IR (neat) 3105, 2940, 2820, 2005, 1950, 1605, 1430, 1420, 1355, 1250, 1190, 1155, 1110, 1085, 1015, 1000, 965, 915, 860, 830, 710, 625, 620, 580, 500 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 254.0 (bridging-CO), 214.6 and 213.7 (Fe-CO), 152.5 (C_1), 139.4 (C_2), 86.1 (Cp), 71.7 (C_6), 56.7 (OMe), 26.3, 25.4, and 16.8 (C_3-C_5); MS m/e 288.0471 (M^+-CO, Calcd. 288.0448); Anal. Found: C, 57.11; H, 5.14. Calcd. for $C_{15}H_{16}FeO_4$: C, 56.99, H. 5.10%.

Dicarbonyl-η^5-cyclopentadienyl-η^1-(6-methoxy-1-cyclohexenyl)iron (126).

Dicarbonyl-η^5-cyclopentadienyl(6-methoxycyclohexene-1-carbonyl)-iron (1.46 g; 0.0046 moles) was dissolved in d_6-acetone (2 mL) under a N_2 atmosphere. This was filtered into an NMR tube which was then photolyzed under a N_2 atmosphere for 2 hours at 0°C. The product was then coated on an alumina (neutral; grade II) and then chromatographed on an alumina (neutral; grade II) column (½ inch × 2 inches) eluting with hexane. Only one yellow band was collected and removal of the solvent gave 0.926 g (70%) of a yellow, air-sensitive oil (can be stored for only ~1 day under a N_2 atmosphere; best to use right after generating the complex). An analytical sample was prepared by further chromatographing the yellow oil on a second column (½ inch × 1 inch; elution with hexane) to afford a yellow, air-sensitive oil: ^{1}H NMR (d_6-benzene; Figure 23) δ 6.80 (m, H_2, 1H), 4.35 (s, Cp, 5H), 3.40 (m, H_6, 1H), 3.20 (s, OMe, 3H), 2.15 (m, CH_2's, 2H), 1.70 (m, CH_2's, 4H); IR (neat) 3100, 2920, 2840, 2000, 1945, 1430, 1350, 1330, 1190, 1150, 1080, 990, 930, 830, 790, 630 cm^{-1}; decoupled ^{13}C NMR ($CDCl_3$) δ 216.9 (Fe-CO), 140.2 (C_1), 139.4 (C_2), 85.9 (C_6), 85.5 (Cp), 56.0 (OMe), 30.9, 29.1, 18.7 (C_3-C_5); MS m/e 288 (M^+), 260 (M^+-CO), 232 (M^+-2CO); Anal. Found: C, 54.55; H, 5.37. Calcd. for $C_{14}H_{16}FeO_3$: C, 58.36; H, 5.60%.

Reaction of Dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron (72) with Trimethylsilyl Trifluoromethanesulfonate Followed by the Addition of Ethanol.

To a dry Schlenk tube (equipped with a magnetic stirrer) was added a mixture of dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron (0.187 g; 0.6 mmoles) in CH_2Cl_2 (15 mL). This was cooled to -78°C at which time a cold (-78°C) mixture of $Me_3SiOSO_2CF_3$ (0.15 g; 0.65 mmoles) in CH_2Cl_2 (15 mL) was added dropwise over 2 minutes under a N_2 atmosphere by syringe. This reaction mixture was allowed to stir for 2.5 hours (at -78°C) at which time a cold (-40°C) mixture of absolute ethanol (30 mL) and Na_2CO_3 (20 mg) was added rapidly by means of a transfer needle. After stirring for 3 hours at -78°C the reaction was allowed to stir 5 hours at room temperature. The reaction mixture was then coated on alumina (neutral; grade II) and then chromatographed on an alumina (neutral; grade II) column (½ inch × 3 inches) elution with hexane (done in a dry box). Only one yellow band was collected. Removal of the solvent gave 0.105 g (54%) of a brownish, air-sensitive oil: The ^1H NMR (Figure 11) and IR spectral properties are in accord with dicarbonyl-η^5-cyclopentadienyl-η^1-(7-ethoxy-1-cycloheptenyl)iron (as previously reported).

Reaction of Dicarbonyl-η^5-cyclopentadienyl-η^1-(6-methoxy-1-cyclohexenyl)-iron (126) with Trimethylsilyl Trifluoromethanesulfonate Followed by the Addition of Ethanol.

To a dry Schlenk tube (equipped with a magnetic stirrer) was added a mixture of dicarbonyl-η^5-cyclopentadienyl-η^1-(6-methoxy-cyclohexenyl)-iron (0.3998 g; 1.4 mmoles) in CH_2Cl_2 (10 mL). This was cooled to -78°C

at which time a cold mixture of $Me_3SiOSO_2CF_3$ (0.33 g; 1.4 mmoles) in CH_2Cl_2 (10 mL) was added dropwise over 2 minutes by syringe. This was allowed to stir for 2 minutes at -78°C at which time a cold (-40°C) mixture of absolute ethanol (15 mL) and Na_2CO_3 (~10 mg) was rapidly added by the use of a transfer needle. After stirring for 3 hours (at -78°C) the reaction mixture was allowed to stir for 1 hour at room temperature. The products were coated on alumina (neutral; grade II; under a N_2 atmosphere) and chromatographed on an alumina (neutral; grade II) column (½ inch × 4 inches) elution with hexane (in a dry box). Only one yellow band was collected and removal of the solvent gave 60 mg (15%) of a yellow, air-sensitive solid: The ^1H NMR and IR spectral properties are in accord with the known product dicarbonyl-η^5-cyclopentadienyl(cyclohexene)iron (95) as previously reported.

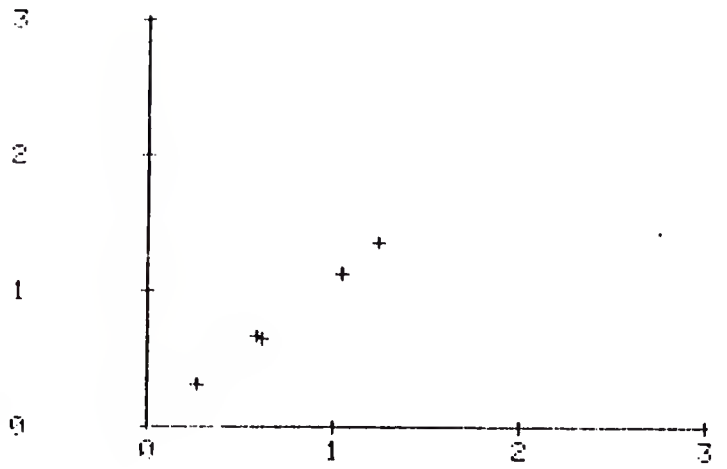
Treatment of Dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron (72) with $Me_2SiOSO_2CF_3$.

To a dry Schlenk tube (equipped with a magnetic stirrer) was added dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron (0.9087 g; 0.003 moles) in CH_2Cl_2 (20 mL). This mixture was cooled to -78°C at which time a cold (-78°C) mixture of $Me_3SiOSO_2CF_3$ (0.998 g; 0.004 moles) in CH_2Cl_2 (10 mL) was added dropwise over 4 minutes under a N_2 atmosphere; after 3 minutes a yellow solid could be seen. The reaction mixture was allowed to stir for 30 minutes at -78°C followed by 25 minutes at room temperature at which time the solvent was removed in vacuo to afford a brown solid. The solid was dissolved in d_6-acetone (Figure 5) and then added to a 25 mL round bottom flask. To this was added a small amount of dry NaI, all done in a dry box, followed by

stirring the solution for 5 minutes at which time the brownish solution immediately turned to a purplish color (Figure 6). This was then distilled [bulb (room temperature) to bulb (-196°C); 0.5 torr] to afford a clear liquid in the bulb at -196°C and a solid (0.3802 g; 42%) in the bulb at room temperature. The solid was dicarbonyl-η^5-cyclopentadienyliron iodide, FpI: ^{1}H NMR (d_6-acetone) δ 5.20 (s).

By GC/MS the clear liquid was shown to be a mixture of cycloheptene (81) and 1,3-cycloheptadiene (82). To determine the amounts of the two a calibration curve was used. Here a measured amount of toluene (internal standard) was added to known amounts of cycloheptene (81) and 1,3-cycloheptadiene (82). The weights were recorded and the mixture was analyzed by glpc (Column A; column temp. 95°C; detector temp. 210°C; injector temp. 200°C; filament current 150 milliamperes D.C.; flow rate 40 mL/min.). In this fashion, 5 samples containing different weight ratios were analyzed. After the analysis, the weight ratios were calculated and a plot (Figure 26) was made of the weight ratios vs. area ratios:

Sample #	Weight of Cycloheptene	Weight of Toluene	Weight Ratio ene/toluene	Area Ratio ene/toluene
1	0.7316 g	0.5404 g	1.35	1.24
2	0.6804 g	1.0385 g	0.66	0.59
3	0.2561 g	0.7919 g	0.32	0.27
4	0.4891 g	0.7594 g	0.64	0.62
5	0.7300 g	0.6268 g	1.12	1.04

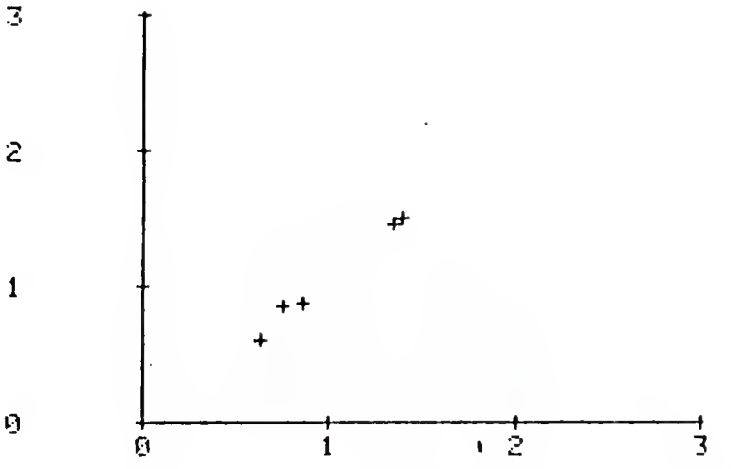


AOV: LINEAR REG:CODE 1

SOURCE	DF	SS	MS	F
TOTAL	4	0.7		
REG	1	0.7	0.7	999.9
RESID	3	0.0	0.0	

R SQUARE = 0.997

YHAT = 0.017 + 1.065 X



AOV: LINEAR REG:CODE 1

SOURCE	DF	SS	MS	F
TOTAL	4	0.6		
REG	1	0.6	0.6	231.1
RESID	3	0.0	0.0	

R SQUARE = 0.987

YHAT = -0.067 + 1.122 X

Figure 26. Calibration curve of (a) cycloheptene; (b) 1,3-cycloheptadiene.

Sample #	Weight of diene	Weight of Toluene	Weight Ratio diene/toluene	Area Ratio diene/toluene
1	0.8122 g	0.5404 g	1.50	1.40
2	0.8945 g	1.0385 g	0.86	0.76
3	0.4823 g	0.7919 g	0.61	0.64
4	0.6592 g	0.7594 g	0.87	0.86
5	0.9072 g	0.6268 g	1.45	1.35

To the clear liquid (from above) was added 0.0305 g of toluene. Analysis (glpc) gave:

Unknown	Weight of Toluene	Area Ratio diene/toluene	Area Ratio ene/toluene
1	0.0305 g	5.05	1.00

With the help of the prepared calibration curve (Figure 26) it was found that the weights were 1,3-cycloheptadiene (0.1708 g; 60%) and cycloheptene (0.0329 g; 11%).

Treatment of Dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron (72) with $HBF_4 \cdot Et_2O$.

To a dry Schlenk tube (equipped with a magnetic stirrer) was added dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron (0.8977 g; 0.003 moles) in diethyl ether (15 mL). This mixture was cooled to -78°C at which time a cold (0°C) mixture of $HBF_4 \cdot Et_2O$ (0.821 g) in diethyl ether (10 mL) was added dropwise under a N_2 atmosphere. The reaction mixture was allowed to stir for 5 minutes at -78°C (a solid was formed) followed by 30 minutes at room temperature. The precipitate was

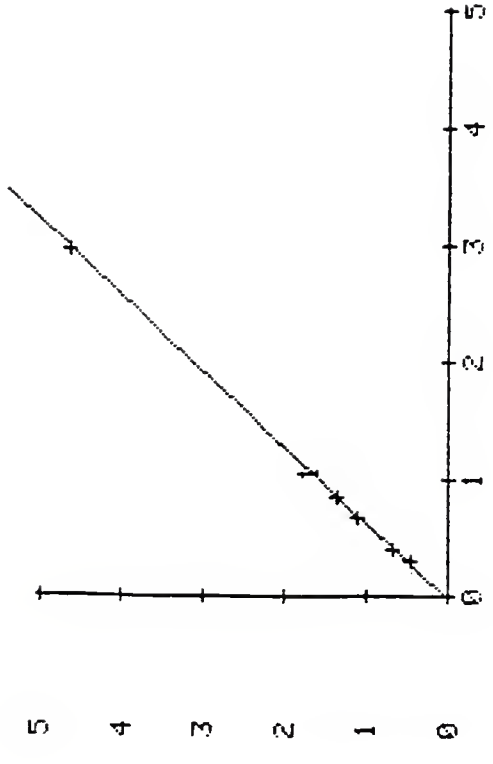
filtered in a dry box and the solid was dried under vacuum for 3 hours. The yellow solid was dissolved in d_6-acetone (Figure 3) and then added to a 25 mL round bottom flask. To this was added a small amount of dry NaI (all done in a dry box) followed by stirring the solution for 5 minutes at which time the solution immediately turned to a purplish color. This was then distilled [bulb (room temperature) to bulb (-196°C); 0.5 torr] to afford a clear liquid in the bulb at -196°C and a solid (0.4862 g; 53%) in the bulb at room temperature. The solid was FpI: ^{1}H NMR (d_6-acetone) δ 5.20 (s).

By GC/MS the clear liquid was shown to be a mixture of cycloheptanone (80), cycloheptene (81) and a small amount of 1,3-cycloheptadiene (82). To determine the amounts of the two a calibration curve (Figure 27) was used again (same conditions as used in the previous experiment).

Sample #	Area Ratio one/toluene	Weight Ratio one/toluene
1	0.29	0.47
2	0.67	1.09
3	0.86	1.35
4	2.96	4.63
5	0.41	0.67

To the clear liquid from above was added 0.0278 g of toluene. Analysis (glpc) gave:

Unknown	Weight of Toluene	Area Ratio ene/toluene	Area Ratio one/toluene
1	0.0278 g	3.95	2.94



ANOV: LINEAR REG:CODE 1

SOURCE/DF	SS	MS	F
TOTAL 4	11.6		
REG 1	11.6	11.6	999.9
RESID 3	0.0	0.0	

R SQUARE = 1.000

YHAT = 0.028 + 1.555 X

Figure 27. Calibration curve of cycloheptanone.

With the help of the prepared calibration curve (Figures 26 and 27) it was found that the weights were cycloheptene (0.1173 g; 41%) and cycloheptanone (0.1279 g; 38%).

Treatment of (72) with $Me_3SiOSO_2CF_3$ Followed by the Addition of Fp Anion.

To a dry Schlenk tube (equipped with a magnetic stirrer) was added a mixture of dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron (0.4068 g; 0.001 moles) in CH_2Cl_2 (10 mL). This was cooled to -78°C at which time a cold (-78°C) solution of $Me_3SiOSO_2CF_3$ (0.30 g; 0.001 moles) in CH_2Cl_2 (10 mL) was added dropwise over 10 minutes by syringe under a N_2 atmosphere. The reaction mixture was allowed to stir for 1 hour at -78°C followed by the removal of the solvent in vacuo at 0°C to afford a tan solid. To the tan solid was added THF (20 mL) followed by cooling the mixture to -78°C. This was allowed to stir for 10 minutes at which time Fp anion (0.40 g; 0.002 moles) was added by employing a solid addition funnel. After 30 minutes at -78°C the mixture was allowed to stir for 1 hour at room temperature. The solvent was removed to afford a brownish oil [the solvent that was removed showed small traces of cycloheptene (81) and cycloheptadiene (82) by GC/MS]. The products were coated on alumina (neutral; grade II; under a N_2 atmosphere) and chromatographed on an alumina (neutral; grade II) column (½ inch × 3 inches) eluting first with hexane [no dimer (113) was collected or any other products] then with CH_2Cl_2. A reddish band was collected and removal of the solvent afforded 0.3290 g (68%) of FpI: ^1H NMR (d_6-acetone) δ 5.20 (s, Cp).

Treatment of (72) with $Me_3SiOSO_2CF_3$ Followed by the Addition of Tetrabutylammonium Iodide.

To a dry Schlenk tube (equipped with a magnetic stirrer) was added a mixture of dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron (0.5965 g; 1.9 mmoles) in CH_2Cl_2 (20 mL). This was cooled to -78°C at which time a cold (-78°C) mixture of $Me_3SiOSO_2CF_3$ (0.45560 g; 2.0 mmoles) in CH_2Cl_2 (4 mL) was added dropwise under a N_2 atmosphere. The reaction mixture was allowed to stir 15 minutes at -78°C at which time a cold (0°C) solution of tetrabutylammonium iodide (1.85 g; 5.0 mmoles) in CH_2Cl_2 (20 mL) was added by using a transfer needle. This was allowed to stir for 1.5 hours at -78°C [low temperature ^1H NMR shows no reaction] followed by 1.5 hours at room temperature. The products were coated on alumina (neutral; grade II) under a N_2 atmosphere and chromatographed on an alumina (neutral; grade II) column (½ inch × 5 inches; done in a dry box) elution first with hexane [no dimer (113) was collected or any other products) then with CH_2Cl_2. A brownish band was collected and removal of the solvent gave 0.3755 g (63%) of FpI: ^1H NMR (d_6-acetone) δ 5.20 (s).

Reaction of (72) with $Me_3SiOSO_2CF_3$: Isolation of Allene Complex (35).

To a dry Schlenk tube (equipped with a magnetic stirrer) was added a mixture of dicarbonyl-η^5-cyclopentadienyl-η^1-(7-methoxy-1-cycloheptenyl)iron (0.8082 g; 2.7 mmoles) in CH_2Cl_2 (10 mL). This was allowed to stir for 10 minutes at -78°C under a N_2 atmosphere at which time a cold (-78°C) mixture of $Me_3SiOSO_2CF_3$ (0.621 g; 2.7 mmoles) in CH_2Cl_2 (5 mL) was added slowly by syringe. This was allowed to stir 30 minutes

at -78°C at which time the cold bath was changed to ice water and a full vacuum (0.5 torr) was applied. After 15 minutes a tan solid was left. This was then dissolved in CH_2Cl_2 (10 mL) and cooled to -78°C at which time dry diethyl ether (10 mL) was added by syringe. A precipitate formed and after 2 hours (at -78°C) the mixture was warmed to room temperature (no longer than 15 minutes because the solid is not stable in CH_2Cl_2) and the precipitate was filtered in a dry box. The tan solid was washed 2 times with dry diethyl ether (10 mL) and then dried for 30 minutes under vacuum (0.5 torr). This afforded 0.7954 g (71%) of a tan, air-sensitive solid which can be stored for at least 6 weeks under a N_2 atmosphere at -78°C, mp. 77°-79°C (decomposes) in a sealed cap. tube: ^1H NMR (d_6-acetone; at -20°C; Figure 12; stable in acetone only at low temperature) δ 6.55 (m, H_3, 1H), 5.95 (s, Cp, 5H), 4.45 (m, H_1, 1H), 2.30 (m), 2.00 (m), 1.00 (m); [^1H NMR (d_6-acetone) after being at room temperature 1 hour, Figures 28 and 29]; IR (d_6-acetone) 2080, 2040 cm^{-1}; decoupled ^{13}C NMR (d_6-acetone) 209.6, 206.6 (Fe-CO's), 150.1 (C_2), 124.3 (C_3), 91.9 (Cp), 42.6 (C_1), other C's (C_4-C_7) under acetone; ^1H NMR (CD_3NO_2; stable in solution for at least 4 hours at room temperature; Figure 30) δ 6.61 (m, H_3, 1H), 5.77 (s, Cp, 5H), 4.34 (m, H_1, 1H), 2.4 (m), 2.01 (m), 0.95 (m); IR (CD_3NO_2) 2075, 2040 cm^{-1}; decoupled ^{13}C NMR (CD_3NO_2; Figure 13) δ 210.2, 207.2 (Fe-CO's), 150.1 (C_2), 125.8 (C_3), 92.3 (Cp), 43.6 (C_1), 30.7, 29.6, 29.4 (C_4-C_7); Anal. Found: C, 42.63; H, 3.63. Calcd. for $C_{15}H_{15}FeF_3O_5S$: C, 42.88; H, 3.60%.

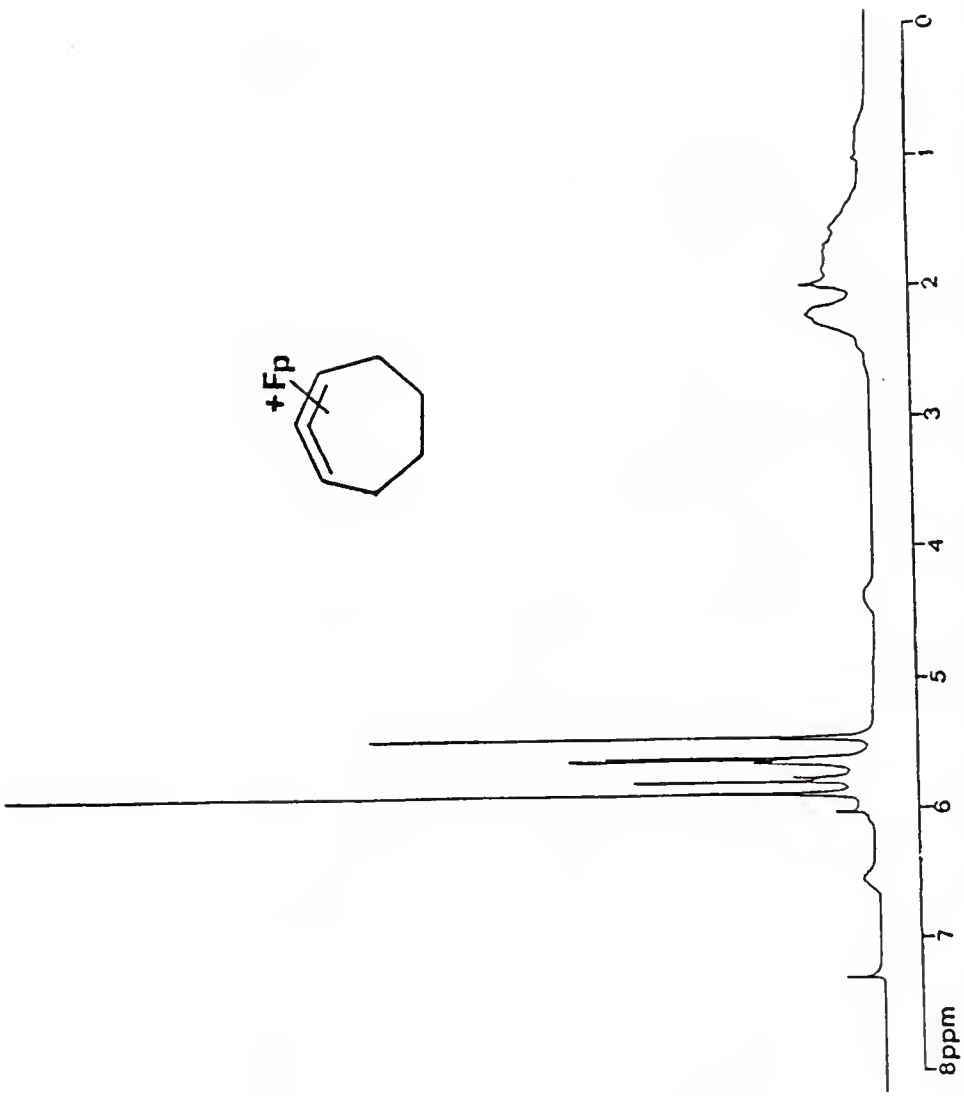


Figure 28. ^1H NMR spectrum of (35) in d_6-acetone at -20°C after one hour at room temperature.

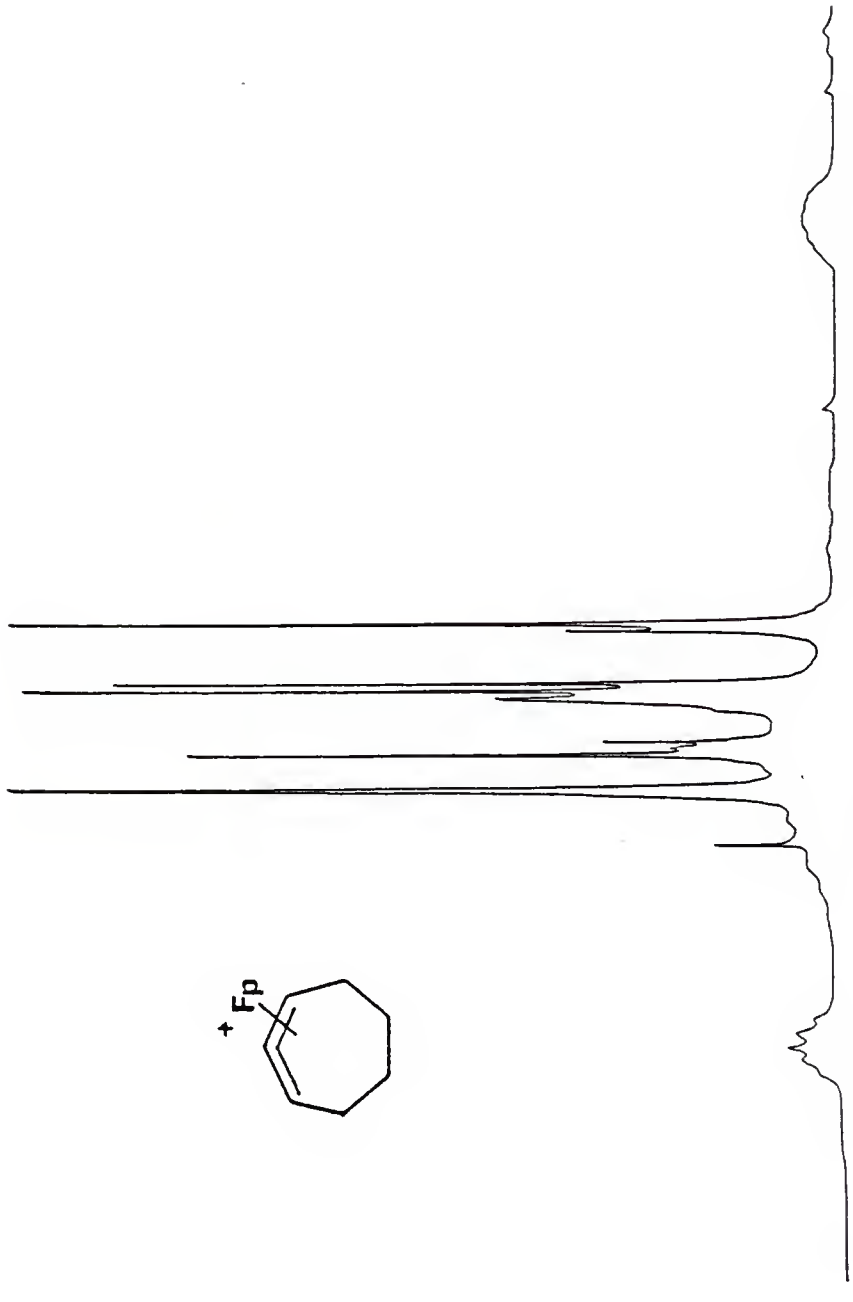


Figure 29. An expansion of the ^1H NMR spectrum of (35) in d_6-acetone at -20°C after one hour at room temperature in d_6-acetone.

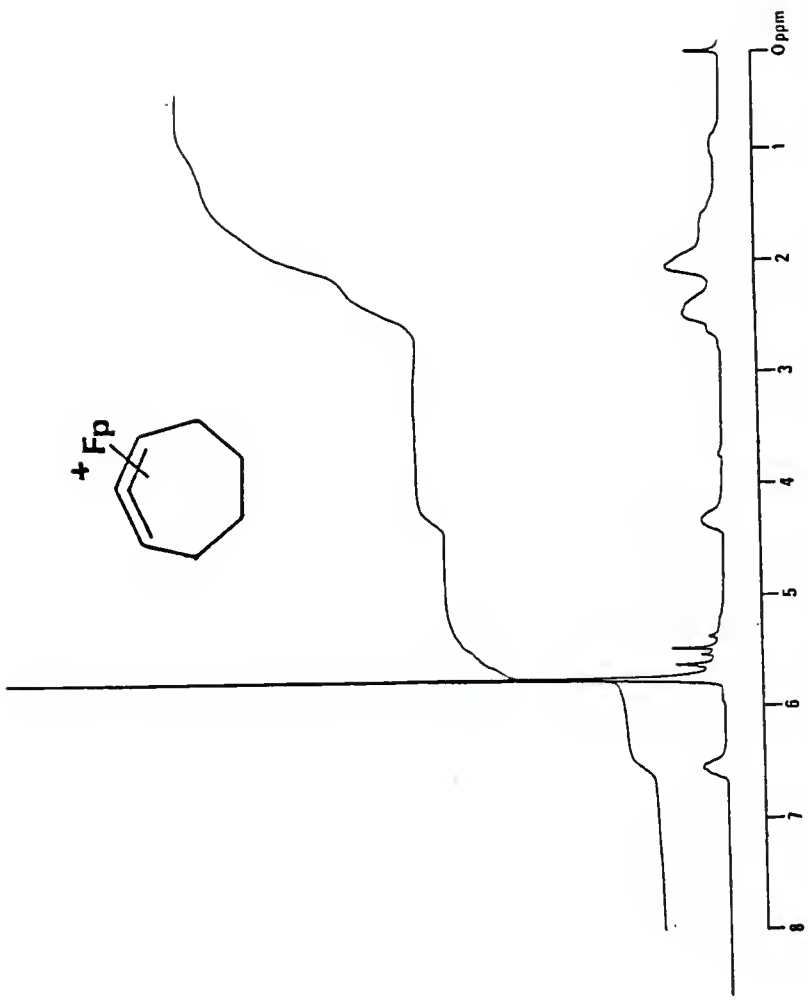


Figure 30. ^1H NMR spectrum of (35) in CD_3NO_2 at -20°C.

Treatment of (35) with NaI in d_6-Acetone.

To a dry Schlenk tube (equipped with a magnetic stirrer) was added dicarbonyl-η^5-cyclopentadienyl-η^2-(1,2-cycloheptadiene)iron trifluoromethanesulfonate (0.302 g; 0.7 mmoles) and dry NaI (0.20 g). To the reaction mixture was added 2 mL of cold (0°C) d_6-acetone followed by cooling the mixture to -78°C. This was then allowed to stir 2 hours at -78°C followed by 4 hours at room temperature (Figure 18). The reaction mixture was then distilled [bulb (room temperature) to bulb (-196°C); 0.5 torr] to afford a clear liquid in the bulb at -196°C and a solid (0.1350 g; 61%) in the bulb at room temperature. The solid was FpI: ^{1}H NMR (d_6-acetone) δ 5.20 (s).

The clear liquid was analyzed by glpc to reveal a mixture of cycloheptene (81) and 1,3-cycloheptadiene (82). Further analysis (glpc) of the liquid gave:

Unknown	Weight of Toluene	Area Ratio ene/toluene	Area Ratio diene/toluene
1	0.0133 g	1.10	2.50

With the help of the prepared calibration curve (Figure 26) it was found that the weights were cycloheptene (0.04 g; 20%) and cycloheptadiene (0.0333 g; 49%).

Decomposition of (35) in the Air.

The allene complex [(35); 0.1840 g; 0.4 mmoles] in a 25 mL round bottom flask was exposed to the air. After 20 minutes the tan solid changed to a dark, brownish oil. The oil was dissolved in d_6-acetone

[^{1}H NMR (d_6-acetone); room temperature; Figure 21] at which time a small amount of dry NaI was added. After 5 minutes the solution turned to a purplish color. The reaction mixture was then distilled [bulb (room temperature) to bulb (-196°C); 0.5 torr] to afford a clear liquid in the bulb at -196°C and a solid (0.0951 g; 75%) in the bulb at room temperature. The solid was FpI: ^{1}H NMR (d_6-acetone) δ 5.20 (s).

The clear liquid was analyzed by GC/MS to reveal trace amounts of cycloheptene (81), 1,3-cycloheptadiene (82), and a large amount of cycloheptanone (80). Analysis (glpc) of the liquid gave:

Unknown	Weight of Toluene	Area Ratio one/toluene
1	0.0115 g	2.40

With the help of the prepared calibration curve (Figure 27) it was found that the weight of cycloheptanone (80) was 0.0432 g (88%).

Decomposition of (35) in CH_2Cl_2.

To the allene complex [(35); 0.2810 g; 0.7 mmoles] in a 25 mL round bottom flask was added 15 mL of CH_2Cl_2. This was allowed to stir 4 hours at room temperature at which time the solvent was removed in vacuo to leave a brownish oil. This oil was dissolved in d_6-acetone followed by the addition of dry NaI. After 2 minutes the solution turned to a purplish color. This was then distilled [bulb (room temperature) to bulb (-196°C); 0.5 torr] to afford a clear liquid in the bulb at -196°C and a solid in the bulb at room temperature. The solid was FpI: ^{1}H NMR (d_6-acetone) δ 5.20 (s).

The clear liquid was analyzed by glpc to reveal trace amounts of cycloheptene (81) and a large amount of 1,3-cycloheptadiene (82). Analysis (glpc) of the liquid gave:

Unknown	Weight of Toluene	Area Ratio diene/toluene
1	0.0421 g	0.57

With the help of the calibration curve (Figure 26) it was found that the weight of 1,3-cycloheptadiene was 0.0241 g (40%).

Decomposition of (35) in CH_2Cl_2 in the Presence of Ph_3CH.

The allene complex [(35); 0.2701 g; 0.6 mmoles] was dissolved in a solution of CH_2Cl_2 (20 mL) and excess Ph_3CH at -78°C. This mixture was allowed to stir for 30 minutes at -78°C followed by 3 hours at room temperature. The solvent was removed to afford a brownish oil. The oil was dissolved in d_6-acetone (Figure 19) followed by the addition of NaI (Figure 20). This was then distilled [bulb (room temperature) to bulb (-196°C); 0.5 torr] to afford a clear liquid in the bulb at -196°C and a solid in the bulb at room temperature. The solid was FpI: ^1H NMR (d_6-acetone) δ 5.20 (s).

The clear liquid was analyzed by GC/MS to reveal cycloheptene (81) and 1,3-cycloheptadiene (82). Analysis (glpc) of the liquid gave:

Unknown	Weight of Toluene	Area Ratio ene/toluene	Area Ratio diene/toluene
1	0.0531 g	.37	.57

With the help of the prepared calibration curve (Figure 26) it was found that the weights were 1,3-cycloheptadiene (0.031 g; 51%) and cycloheptene (0.021 g; 34%).

Dicarbonyl-η^5-cyclopentadienyl-η^2-(1,2-cyclononadiene)iron Hexafluorophosphate (23).

To a dry 50 mL round bottom flask (equipped with a magnetic stirrer) was added dicarbonyl-η^5-cyclopentadienyl-η^2-(cyclohexene)iron hexafluorophosphate (0.502 g; 0.002 moles), 1,2-cyclononadiene (0.3092 g; 0.003 moles) and CH_2Cl_2 (50 mL). This was refluxed for 1.5 hours under a N_2 atmosphere after which time the mixture was allowed to cool to room temperature. To the reaction mixture was added diethyl ether (200 mL). After 10 minutes the solution was filtered to leave 0.5139 g (92%) of a yellow solid: ^1H NMR (CD_3NO_2; room temperature; Figure 8) δ 6.5 (m, H_3, 1H), 5.80 (s, Cp, 5H), 4.45 (m, H_1, 1H), 3.00-1.00 (m); IR (CD_3NO_2) 2080, 2040 cm^{-1}; ^{13}C NMR decoupled (CD_3NO_2; Figure 14; room temperature) δ 210.5, 209.5 (Fe-CO's), 148.5 (C_2), 122.3 (C_3), 92.0 (Cp), 51.3 (C_1), 34.2, 32.6, 28.5, 26.1, 20.7 (C_4-C_9).

Treatment of (126) with $Me_3SiOSO_2CF_3$.

To a dry Schlenk tube (equipped with a magnetic stirrer) was added dicarbonyl-η^5-cyclopentadienyl-η^1-(6-methoxy-1-cyclohexenyl)iron [(126); 0.4101 g; 0.001 moles] in CH_2Cl_2 (15 mL). This mixture was cooled to -78°C at which time a cold (-78°C) mixture of $Me_3SiOSO_2CF_3$ (0.3210 g; 0.001 moles) in CH_2Cl_2 (10 mL) was added dropwise over 2 minutes under a N_2 atmosphere. This mixture was allowed to stir 30 minutes at -78°C

followed by 2 hours at room temperature. Removal of the solvent in vacuo left a brownish oil. The oil was dissolved in d_6-acetone, (Figure 24) followed by the addition of excess NaI to give an immediate color change (brown to purple). This was then distilled [bulb (room temperature) to bulb (-196°C); 0.5 torr] to afford a clear liquid in the bulb at -196°C and a solid in the bulb at room temperature. The solid was FpI: ^{1}H NMR (d_6-acetone) δ 5.20 (s).

By GC/MS the clear liquid was shown to be a mixture of cyclohexene (132) and 1,3-cyclohexadiene (133). To determine the amounts of the two a calibration curve was used. Here a measured amount of toluene (internal standard) was added to known amounts of cyclohexene and 1,3-cyclohexadiene. The weights were recorded and the mixture was analyzed by glpc (Column A; column temp. 80°C; detector temp. 200°C; injector temp. 200°C; flow rate 40 mL/min.). In this fashion, 5 samples containing different weight ratios were analyzed. After the analysis, the weight ratios were calculated and a plot (Figure 31) was made of the weight ratios vs. area ratios:

Sample #	Weight Ratio ene/toluene	Area Ratio ene/toluene
1	2.00	2.43
2	1.28	1.42
3	0.401	0.43
4	0.699	0.792
5	0.693	0.789

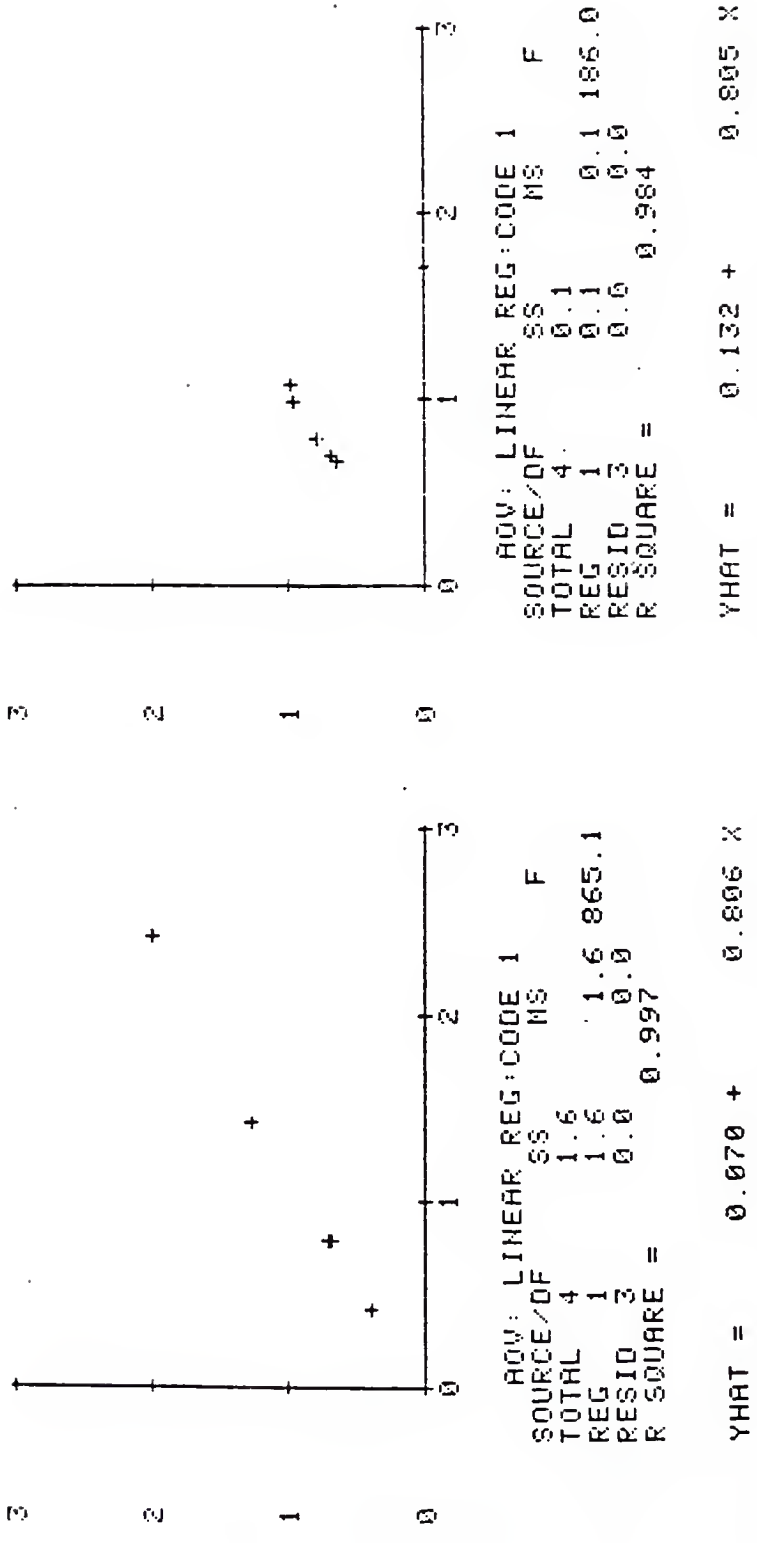


Figure 31. Calibration curve of (a) cyclohexene; (b) 1,3-cyclohexadiene.

Sample #	Weight Ratio diene/toluene	Area Ratio diene/toluene
1	0.98	1.08
2	0.95	0.99
3	0.686	0.70
4	0.783	0.78
5	0.654	0.66

To the clear liquid (from above) was added 0.0165 g of toluene. Analysis (glpc) gave:

Unknown	Weight of Toluene	Area Ratio diene/toluene	Area Ratio ene/toluene
1	0.0165 g	.66	2.57

With the help of the prepared calibration curve (Figure 31) it was found that the weights were 1,3-cyclohexadiene (0.0109 g; 10%) and cyclohexene (0.0353 g; 30%).

APPENDIX

LIST OF REAGENTS PURCHASED FROM SPECIFIC CHEMICAL SUPPLY HOUSES

Dicarbonylcyclopentadienyliodoiron - Alfa

n-Butyllithium (1.6 M in hexane) - Aldrich

1,3-Cyclohexadiene (96%) - Aldrich

Cyclohexene (99%) - Aldrich

Cycloheptene (99%) - Aldrich

2-Cyclohexen-1-one - Aldrich

Cycloheptanone (97%) - Aldrich

1,3-Cycloheptadiene (97%) - Aldrich

Cyclopropanecarboxylic acid chloride - Aldrich

K-Selectride - Aldrich

d_6-acetone - Aldrich

d_6-benzene - Merck Sharp & Dohme

$CDCl_3$ - Merck Sharp & Dohme

CD_2Cl_2 - Merck Sharp & Dohme

CD_3NO_2 - Merck Sharp & Dohme

Silver nitrate - Alfa

Silver perchlorate - Alfa

Iodomethane - Aldrich

1-Cyclohexenecarbonyl Chloride - Frinton Laboratories

Tetrafluoroboric acid-diethyl ether complex - Aldrich

Trimethylsilyl trifluoromethanesulfonate - Aldrich

Trimethyl phosphite - Aldrich

Iron pentacarbonyl - Aldrich

Aldrich Chemical Co.
P.O. Box 355
Milwaukee, Wisconsin 53201

Alfa Products-Thiokol/Ventron Division
P.O Box 299
152 Andover St.
Danvers, Massachusetts 01923

Frinton Laboratories, Inc.
P.O Box 2310
Vineland, N.J. 08360

Merck Sharp and Dohme

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BIOGRAPHICAL SKETCH

Frank John Manganiello was born March 16, 1954, in Chicago, Illinois. At the age of twelve, he and his parents moved to Port Charlotte, Florida. He attended Charlotte High School in Punta Gorda.

In September, 1973, he began undergraduate work at Murray State University in Murray, Kentucky. In 1975, he transfered to the University of Florida where he received his B.S. degree in 1977.

While attending Murray State University, he married the former Miss Colleen McLaughlin. In 1974 his daughter Wendy Ann Manganiello was born followed by Micah Paul Manganiello in 1979.

In September, 1977, he began graduate work at the University of Florida in Gainesville, Florida, and in 1980 received his M.S.. Upon completion of the dissertation, he will begin work as a senior research chemist at 3M, Saint Paul, Minnesota.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William M. Jones, Chairman
Professor of Chemistry

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Merle A. Battiste
Professor of Chemistry

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Professor of Chemistry

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December 1982

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